CANADIAN WATER QUALITY GUIDELINES

prepared by the
Task Force on Water Quality Guidelines
of the
Canadian Council of Resource
and
Environment Ministers

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Note to Readers

Experts in any field discussed in this document are invited to make available to the Canadian Council of Resource and Environment Ministers comments or important published information for consideration in subsequent updates of the Canadian Water Quality Guidelines.

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Preface

Water quality guidelines and objectives are used by Canadian provincial, territorial and federal agencies in their efforts to assess water quality problems and to manage competing uses of water resources. Recognizing the increasing importance of water quality guidelines in this process, the Canadian Council of Resource and Environment Ministers asked its Task Force on Water Quality Guidelines to prepare water quality guidelines relevant to Canadian conditions.

In preparing this document, the Task Force reviewed the water quality guidelines for inland waters available from Canadian and other sources. These guidelines were reviewed for applicability in Canada and adapted to suit Canadian conditions where necessary. The information gaps identified during the development of the guidelines were noted and reported to Council as research priorities. The guidelines will be updated as new information becomes available.

It must be emphasized that these guidelines do not constitute values for uniform national water quality and that their use will require consideration of local conditions.

Acknowledgements

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Introduction

Canadians are concerned about the quality of their water resources and are confronted by a number of problems threatening these resources. One obstacle in assessing the magnitude of these problems is the difficulty of defining acceptable water quality for specific uses. Faced with the task of managing these waters, many provincial, territorial and federal agencies consult water quality guidelines, from various Canadian and foreign sources, to assess water quality and to develop site-specific water quality objectives.

At the 1983 annual meeting of the Canadian Council of Resource and Environment Ministers (CCREM), a Task Force on Water Quality Guidelines was established and asked to:

1. inventory water quality criteria and guidelines used by governments throughout Canada;
2. review and make recommendations to Council on the desirability of, and possibilities for, a harmonization of guidelines throughout Canada; and
3. identify emerging issues in the area of water quality and assess the ability of current criteria and guidelines to deal with these issues.

The Task Force tabled their report at the 1984 annual CCREM meeting and recommended harmonized Canadian water quality guidelines. This recommendation met with the Council's approval and the Task Force was asked to prepare the Canadian Water Quality Guidelines.

The Canadian Water Quality Guidelines were developed to provide basic scientific information about the effects of water quality parameters on uses in order to assess water quality issues and concerns and to establish water quality objectives for specific sites.

In approaching this work, the members of the Task Force found that the use of the terms criteria, guideline, objective and standard varies according to the individual agency. For the purposes of this document, these terms will be defined as follows:

1. **Criteria**: scientific data evaluated to derive the recommended limits for water uses.
2. **Water quality guideline**: numerical concentration or narrative statement recommended to support and maintain a designated water use.
3. **Water quality objective**: a numerical concentration or narrative statement which has been established to support and protect the designated uses of water at a specified site.
4. **Water quality standard**: an objective that is recognized in enforceable environmental control laws of a level of government.

The approach adopted in preparing the Canadian Water Quality Guidelines consisted of a review of existing guidelines from many sources. If these were found appropriate for Canadian environmental conditions, they were adopted as Canadian water quality guidelines. Some published guidelines were found to be inappropriate, but when scientific data were available to modify the guidelines so that they could be used under Canadian conditions, this was done and the guidelines were adopted as Canadian water quality guidelines. For some parameters there were neither appropriate guidelines nor scientific data to modify existing guidelines for Canadian conditions. In this instance, no Canadian water quality guidelines have been recommended. Reviews on a number of water quality parameters, for which there were insufficient data to recommend a guideline, are included to assist in the overall evaluation of water quality. Because the guidelines are recommended based on information currently available, they will be updated as new and relevant data become available.

The following major uses of water are addressed in this document:

- Raw water for drinking water supply
- Recreational water quality and aesthetics
- Freshwater aquatic life
- Agricultural uses
- Industrial water supplies

The guidelines contain recommendations for chemical, physical, radiological and biological parameters necessary to protect and enhance designated uses of water. They apply only to inland surface waters and groundwaters, and not to estuarine and marine waters. The rationale for each parameter is included to assist in the development of water quality objectives to suit local water conditions.

The guidelines should not be regarded as blanket values for national water quality. Variations in environmental conditions across Canada will affect water quality in different ways and many of the guidelines reported here will need to be modified according to these local conditions. Site-specific water quality objectives derived using these guidelines may therefore differ from the recommendations in this document. For waters of superior quality, impairment to guideline concentrations should not be acceptable. Such considerations should form part of the rationale for site-specific water quality objectives.

The Canadian Water Quality Guidelines consist of six chapters and four appendices. The five water uses are dealt with individually in Chapters 1 to 5. For each use, only the parameters of concern to that use have been included. In view of the wide differences in water uses and the water quality concerns associated with each use, the reader will find differences in the approach and format of these chapters. Chapter 6 provides background information on water quality parameters in terms of uses and production; sources and pathways for entering the aquatic environment; environmental concentrations; and forms and fate in the aquatic environment. Not all parameters discussed in Chapter 6 have guidelines for each use. Appendix I is a glossary of terms; Appendix II lists the current and past members of the CCREM Task Force on Water Quality Guidelines; Appendix III lists, by agency, the individuals involved in the production of the guidelines; and, finally, Appendix IV deals with the application of the guidelines.

1.0 RAW WATER FOR DRINKING WATER SUPPLY

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1.0 RAW WATER FOR DRINKING WATER SUPPLY

1.1 INTRODUCTION

Raw public water supplies refer to waters that are used as the intake source of water for public use and can include surface water and groundwater. The majority of Canadians obtain their drinking water from piped water supplies, most of which include some form of treatment between the user and the raw water supply. The purpose of the treatment process is to provide the user with drinking water that is safe, palatable and aesthetically appealing. However, there is a minority of Canadians including individual dwellings in rural communities, farms and also some towns which depend entirely on untreated groundwater.

The Guidelines for Canadian Drinking Water Quality 1978 (Health and Welfare Canada 1979a) were prepared by the Federal-Provincial Advisory Committee on Environmental and Occupational Health. A summary table of maximum acceptable concentrations from this publication is presented in Table 1-1. The drinking water guidelines recommend limits for physical, chemical, radiological and microbiological characteristics of drinking water in terms of maximum acceptable concentrations. Drinking water that contains substances in concentrations greater than these limits either is capable of producing deleterious health effects or is aesthetically objectionable. These drinking water guidelines are currently being revised by the Federal-Provincial Subcommittee on Drinking Water. The final revisions were not available to the CCREM Task Force on Water Quality Guidelines for consideration during the preparation of this document, but will be included in subsequent up-dates.

The Federal-Provincial Subcommittee on Drinking Water advised the Task Force on Water Quality Guidelines that treatment technology is available to produce drinking water from water of almost any quality. Therefore, the Task Force decided that it is not appropriate to recommend numerical guidelines for raw public water supplies at this time.

It must be considered that degradation of raw water quality could result in an increased risk to consumers if health-related constituents are involved. The Task Force on Water Quality Guidelines consider it prudent to protect raw public water supplies to ensure that they are maintained as good sources of drinking water.

Although the drinking water limits presented in Table 1-1 represent drinking water of acceptable quality, there is no inference that one should allow better quality water supplies to be degraded to these limits. The maintenance of good quality drinking water can be achieved both by protecting the raw water supply and by water treatment. It is possible to protect the raw water supply by means of pollution control measures that prevent undesirable constituents from entering the raw water and by good watershed management practices. A wide range of treatment technologies is available by means of which it is possible to produce acceptable drinking water from almost any raw water source.

The following discussion briefly highlights the existing Canadian drinking water guidelines, including information on Canadian exposure and water treatment. The information on exposure and effects has been taken largely from the supporting documentation for the Canadian drinking water guidelines (Health and Welfare Canada 1980). This predates 1978 and is under review as it may not reflect current thinking.

1.2 WATER TREATMENT PROCESSES

Water treatment processes may be operationally divided into two categories: conventional treatment and specialized treatment. Conventional treatment is considered to be processes that are commonly used to condition various surface and groundwater sources. Specialized treatment is used for unusual or uncommon treatment requirements, particularly for the control of specific contaminants such as trace organic chemicals. Table 1-2 summarizes components of treatment processes and their modification of water quality.

For specialized treatment, the main technologies include adsorption, air stripping, ion exchange/removal and oxidation. Adsorption, utilizing such materials as activated carbon or specific synthetic resins, may be used to adsorb particular types of substances, such as organic materials, from the water. Air stripping uses intense aeration to expel volatile or purgeable compounds from water to the air. Oxidation refers to the use of a strong oxidant, such as ozone, for the potential destruction of a particular constituent(s). Other special treatment processes include ion exchange and/or reverse osmosis, which are generally applicable when certain dissolved salts require removal. Conventional treatment processes may also be used successfully in controlling unusual contaminants; examples are preoxidation and coagulation for arsenic removal. A summary of the potential efficiencies of water treatment processes is given in Table 1-3.

1.3 OVERVIEW OF GUIDELINES FOR CANADIAN DRINKING WATER QUALITY 1978

1.3.1 Inorganic Parameters

1.3.1.1 Antimony

1.3.1.1.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 do not recommend a maximum acceptable antimony concentration in drinking water because of an insufficient toxicity data base (Health and Welfare Canada 1979a).

Antimony is not essential to the life and health of humans or other animals (NAS 1980a). The taste threshold for trivalent or pentavalent antimony in water has been given as 0.6 $mg \cdot L^{-1}$ (NAS 1980a; Health and Welfare Canada 1980).

1.3.1.1.2 Canadian Exposure

Although the daily intake of antimony from food has not been estimated for Canadians, the total individual dietary exposure in the United States has been reported as less than 1 $mg \cdot d^{-1}$ (Health and Welfare Canada 1980). Another study reports total exposure from all sources to be only 0.1 mg·d^{-1} (NAS 1982). Drinking water is considered to be a negligible source of antimony intake compared with other foods (Health and Welfare Canada 1980).

Data on antimony concentrations in Canadian drinking water are not readily available. Antimony concentrations in Canadian surface water range from 0.001 to 9.1 mg·L^{-1} (NAQUADAT 1980). Under certain soft-water conditions, antimony may be leached from plumbing materials (Health and Welfare Canada 1980).

1.3.1.1.3 Water Treatment

Little documented information is available on antimony removal by water treatment processes. Because antimony has chemical and biological characteristics similar to those of arsenic (NAS 1980a), treatment processes suitable for arsenic may be applicable. It is anticipated that alum or ferric sulphate coagulation-flocculation in the presence of turbidity and activated carbon adsorption may have some potential for decreasing the concentration of antimony in raw waters.

1.3.1.2 Arsenic

1.3.1.2.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 list the maximum acceptable concentration of arsenic in drinking water as 0.05 mg·L^{-1} (Health and Welfare Canada 1979a).

1.3.1.2.2 Canadian Exposure

In general, Canadian surface waters contain less than 0.05 mg·L^{-1} of total dissolved arsenic. Concentrations greater than 0.05 mg·L^{-1} have been found in groundwater in some parts of Canada (Health and Welfare Canada 1980).

1.3.1.2.3 Water Treatment

The effectiveness of water treatment for arsenic removal is dependent on the valence state of the arsenic in the raw water supply. Conventional coagulation or softening processes have been investigated. It has been generally indicated that the conversion from As(III) to As(V) is desirable and can be accomplished by oxidation using either chlorine or potassium permanganate (Shen 1973; Sorg and Logsdon 1978; U.S. EPA 1978a). Of the common metal coagulants, ferric sulphate was found to be superior to alum for removal. However, both coagulants could reduce concentrations of As(V) in raw waters from fairly high levels to less than 0.05 mg·L^{-1}. Lime softening is quite effective for arsenic removal from hard waters. This removal is dependent on the pH and the arsenic valence. At high pH obtained through the lime treatment process, raw waters containing up to 0.35 mg·L^{-1} As could be effectively treated (Sorg and Logsdon 1978).

In terms of special treatment, it has been found that activated alumina could be effective for arsenic removal (Sorg and Logsdon 1978). This is not a common treatment for surface waters.

For private groundwater supplies, a special process has been developed in Nova Scotia, using chlorination followed by

Table 1-1. Summary – Guidelines for Canadian Drinking Water Quality 1978

Parameter	Maximum acceptable concentration[1] in drinking water (mg·L^{-1})[2,3]
Inorganic Parameters	
Antimony	—
Arsenic	0.05
Asbestos	—
Barium	1.0
Boron	5.0
Cadmium	5 µg·L^{-1}
Chloride	250
Chromium	0.05
Copper	1.0
Cyanide	0.2
Fluoride	1.5
Hardness[4]	—
Iron	0.3
Lead	0.05
Manganese	0.05
Mercury	1 µg·L^{-1}
Nitrate (as N)[5]	10.0
Nitrite (as N)	1.0
pH	6.5-8.5[6]
Selenium	0.01
Silver	0.05
Sulphate	500
Sulphide (as H_2S)	0.05
Total dissolved solids	500
Uranium	0.02
Zinc	5.0
Organic Parameters	
Aldrin + dieldrin	0.7 µg·L^{-1}
Carbaryl[4]	70 µg·L^{-1}
Chlordane (total isomers)	7 µg·L^{-1}
2,4-D	0.1
DDT (total isomers)	0.03
Diazinon	14 µg·L^{-1}
Dieldrin + aldrin	0.7 µg·L^{-1}
Endrin	0.2 µg·L^{-1}
Heptachlor + heptachlor epoxide	3 µg·L^{-1}
Lindane	4 µg·L^{-1}
Methoxychlor	0.1
Methyl parathion	7 µg·L^{-1}
Nitrilotriacetic acid (NTA)	0.05
Parathion	35 µg·L^{-1}
Pesticides (total)[7]	0.1
Phenols	2 µg·L^{-1}
2,4,5-TP	0.01
Toxaphene	5 µg·L^{-1}
Trihalomethanes	0.35
Physical Parameters	
Colour	15 TCU[8]
Odour	—
Taste[4]	—
Temperature[4]	15°C
Turbidity	5 NTU[9]
Radiological Parameters[10]	
^{137}Cs (Cesium)	50 Bq·L^{-1}
^{131}I (Iodine)	10 Bq·L^{-1}
^{226}Ra (Radium)	1 Bq·L^{-1}
^{90}Sr (Strontium)	10 Bq·L^{-1}
^{3}H (Tritium)	40 000 Bq·L^{-1}

Table 1-1. (Cont'd)

Parameter	Maximum acceptable concentration[1] in drinking water ($mg \cdot L^{-1}$)[2,3]
Microbiological Parameters	
Microorganisms	a. No sample should contain more than 10 total coliform organisms per 100 mL; b. not more than 10% of the samples taken in a 30-d period should show the presence of coliform organisms; c. not more than two consecutive samples from the same site should show the presence of coliform organisms; and d. none of the coliform organisms detected should be fecal coliforms.

[1] Maximum Acceptable Concentration (MAC):
Drinking water that contains substances in concentrations greater than these limits is either capable of producing deleterious health effects or is aesthetically objectionable (Health and Welfare Canada 1979a).

[2] Unless otherwise indicated.

[3] Total unless otherwise indicated.

[4] Not discussed in Chapter 1.

[5] Where both nitrate and nitrite are present the total nitrate- plus nitrite-nitrogen should not exceed 10 $mg \cdot L^{-1}$.

[6] Logarithmic scale, no units.

[7] The "total pesticide" limit applies to water in which more than one of the pesticides mentioned in Chapter 1 are present. The sum of their concentrations should not exceed 0.1 $mg \cdot L^{-1}$.

[8] True colour units.

[9] Nephelometric turbidity units.

[10] Becquerel.

Source: Health and Welfare Canada 1979a.

Table 1-2. Water Treatment Processes

Process	Purposes
Aeration	Removal of volatile taste and odour compounds and other dissolved gases (e.g. H_2S, CH_4) Oxygenation and deoxygenation Oxidation (iron)
Presedimentation	Removal of readily settleable particulate matter
Chemical oxidation	Disinfection, biological control Taste and odour control Oxidation of dissolved metals (iron, manganese) Oxidation of some organic chemicals; colour removal enhancement
Coagulation-flocculation	Destabilization of colloidal material and macromolecules and agglomeration of settleable or filterable particulates for the removal of turbidity and colour
Sedimentation	Removal of settleable flocculated particulates prior to filtration
Filtration	Removal of particulates, polishing of water through physical and chemical/biological processes Dual chemical-physical filters (iron and manganese removal)
Softening	Reduction in hardness through the removal of calcium and magnesium by precipitation or ion exchange
Carbon adsorption	Taste and odour control Colour reduction assistance Removal of some organic chemicals including trihalomethane precursors

an exchange medium containing ferric hydroxide. This process can attain high removals at low water flows (Lutwick 1980).

1.3.1.3 Asbestos

1.3.1.3.1 Existing Drinking Water Guideline

No maximum acceptable concentration of asbestos in drinking water was established in the Guidelines for Canadian Drinking Water Quality 1978 as it is believed that the ingestion of asbestos at the concentrations found in drinking water do not constitute a health hazard (Health and Welfare Canada 1979a; NRCC 1982).

1.3.1.3.2 Canadian Exposure

Based on assumed asbestos concentrations and respiratory volumes, the daily intake of asbestos from air has been suggested to be less than 0.6 µg. Because of the paucity of data on asbestos in food and water, dietary intakes can only be approximated. An asbestos intake from water has been calculated at 1.88 ng (2 $L \cdot d^{-1}$ of water containing approximately 1.9×10^6 fibres per litre), considerably less than that from air (Health and Welfare Canada 1980).

A study of selected Canadian drinking water supplies indicated concentrations of asbestos ranging from less than 10^5 to 2×10^9 (chrysotile) fibres per litre in raw water and maximum concentrations of 9.5×10^6 fibres per litre in water treated by filtration (Health and Welfare Canada 1979b; Toft *et al.* 1981).

1.3.1.3.3 Water Treatment

Of the two primary asbestos groups, the amphibole forms are more amenable to treatment than is chrysotile asbestos, which is more prevalent in Canada (NAS 1977; Health and Welfare Canada 1979b). Both conventional and special coagulation-flocculation-filtration treatment process trains are reasonably effective for removal of chrysotile fibres from raw water. Data from existing Canadian facilities have indicated 18- to 300-fold reductions, whereas other pilot and full-scale studies have suggested removals by factors of 10-50 000 (Watkins *et al.* 1978; Toft *et al.* 1981; Hayward 1984).

Because of the measurement technique used, electron microscopy fibre counting, the large numbers generated are not precise, and removal rates should be viewed with some caution. However, with good process control, it is anticipated that target fibre counts in finished water in the $(0.1\text{-}1) \times 10^6$ fibres per litre range could be obtained (Logsdon *et al.* 1983).

Under certain water quality conditions, release of fibres from the erosion of asbestos-cement pipes used in water distribution systems may occur. Water-conditioning measures to make the distributed water less corrosive is a potential mitigation option where problems have been identified (NAS 1982).

Table 1-3. Potential Water Treatment Efficiencies*

	CONVENTIONAL PROCESSES					SPECIAL PROCESSES						
Parameter	Aeration	Chemical oxidation (chlorination, etc.)	Coagulation-flocculation	Lime softening	Filtration	Activated carbon adsorption PAC	Activated carbon adsorption GAC	Air stripping	Demineralizing (reverse osmosis, etc.)	Ion exchange	Ozone	Comments
Aldrin	P		P			G	VG				VG	
Antimony			X		A		X					
Arsenic		A	L-G	G-VG	A	P			G-VG	VG		Valencies important
Asbestos			G-VG		G							
Barium			P	G-VG	A	P	P		VG	VG		
Boron			X				G-VG		X	G-VG		
Cadmium			L-G	VG	A		P-L					pH important
Chlordane		P	L	L		VG	VG					
Chloride									VG	VG		
Chromium			G	G	A	P	P		X	X		Valencies important
Colour			VG		A						VG	
Copper	A		F-G		A							
Cyanide		VG									VG	
2,4-D		P	P		A	VG	X					
DDT		P	L-VG	F		VG	X				P	
Diazinon							X(L)					
Dieldrin			P-L		A		G-VG	L				
Endrin			L			G-VG	VG					
Fluoride									G	G-VG		
Heptachlor						VG	X(VG)					
Heptachlor Epoxide						VG	X					
Iron	A	A		A	VG					VG		
Lead			G-VG	VG	A		X		G-VG	X		
Lindane		P	P		P	G	G-VG					
Manganese		A	L-G	G	A					VG		
Mercury			G	F-G	A	VG	VG					
Methoxychlor			G	G-VG	A	VG	VG					Form important
Methyl Parathion						X	X				X	
Nitrate									F	F-VG		
NTA		P									G-VG	
Odour	A	VG				VG	VG				VG	
Parathion		P-VG	P	P	A	VG	L-VG				G-VG	
pH	A		A	A								
Phenol		G	P			G-VG	X				G-VG	
Radionuclides												
^{226}Ra			P	G-VG	A				VG	G-VG		
^{90}Sr			P	G-VG	A					G-VG		
^{137}Cs				P	P-F				VG	VG		
^{131}I			P	L					VG			
Selenium			P-G	P-F	A				F-G	X		Valencies important
Silver			F-G	G-VG	A		P		X	X		
Sulphate									G-VG	G-VG		
Sulphide	F-VG	F-VG									F-VG	pH important
2,4,5-TP		P	X(F)			X(G)	X(G-VG)					
T. Dissolved Solids									G-VG	G-VG		
Toxaphene		P	P			VG	X(VG)	X				
Trihalomethanes							F-G	F-G				Process generated
Turbidity			G-VG		A							
Uranium			L-G	F-G	A		P			VG		
Zinc			P	F-G	A							

VG = 90-100% removal
G = 70-90% removal
F = 50-70% removal
L = 25-50% removal
P = 0-25% removal
A = auxiliary process

X = possible candidate process (data lacking)
PAC = Powdered activated carbon
GAC = Granular activated carbon
* = Treatment based on available full-scale, pilot or bench studies and should only be used as potential indicators.
Treatability studies and/or site experience should be assessed for specific applications.

Source: McDonald 1986.

1.3.1.4 Barium

1.3.1.4.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend 1.0 mg·L^{-1} as the maximum acceptable concentration of barium (Health and Welfare Canada 1979a). Barium is not considered to be essential for human nutrition. The intake of barium from diet for Canadian adults can be as high as 1.2 mg·d^{-1}. The concentration of 1 mg·L^{-1} could contribute 2 mg·d^{-1} at 2 L·d^{-1} water consumption, and thus increase the total daily intake to 3.2 mg, which is not considered a health hazard upon long-term ingestion (Health and Welfare Canada 1980).

1.3.1.4.2 Canadian Exposure

Food followed by water and air are the three major barium intake vectors. Using a possibly liberal water contribution, the estimated total daily barium intake for Canadians has been projected to be between 0.6 and 1.4 mg (Health and Welfare Canada 1980).

Data on barium concentrations in Canadian drinking water are not readily available (Health and Welfare Canada 1980).

1.3.1.4.3 Water Treatment

Conventional surface water treatment using alum or ferric sulphate coagulation and filtration is not particularly effective, as barium removals during laboratory and pilot studies were only about 30% or less (Sorg and Logsdon 1980). With close pH control, pilot and full-scale lime softening plants have achieved in excess of 90% barium removals (Sorg and Logsdon 1980; Krause and Stover 1982).

Special treatment processes, such as ion exchange using a strong acid cation resin, have been reported to accomplish 94-99% removals in full-scale operations (Sorg and Logsdon 1980; Krause and Stover 1982).

1.3.1.5 Boron

1.3.1.5.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend a maximum acceptable concentration of 5.0 mg·L^{-1} boron (Health and Welfare Canada 1979a). This is based on limiting the daily intake from water to about 10 mg. Boron is not considered to be an essential element for human nutrition (Health and Welfare Canada 1980).

1.3.1.5.2 Canadian Exposure

The total daily boron intake from all environmental sources has been estimated to be 2.4-4.4 mg for Canadians. Food is the primary contributor, with drinking water suggested to provide only about 0.24 mg·d^{-1}, based on median U.S. data. Data are not available on boron concentrations in Canadian drinking water (Health and Welfare Canada 1980).

1.3.1.5.3 Water Treatment

Little information is available on the removal of boron from drinking water, possibly because boron has not been a constituent of concern in water supplies. Potential removal methods include adsorption and demineralization. Granular activated carbon may be capable of 90% removal from raw waters of boron at concentrations not exceeding 5 mg·L^{-1}, but the efficiency decreases with increasing boron concentrations (Choi and Chen 1979a). Demineralization using a special cation-exchange resin or by reverse osmosis may have application for specific situations (Choi and Chen 1979a).

1.3.1.6 Cadmium

1.3.1.6.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 suggest a maximum acceptable cadmium concentration of 5 μg·L^{-1} (Health and Welfare Canada 1979a). The Canadian recommendation is based on health considerations. Food is considered to be the main source of cadmium intake for non-occupationally exposed humans; because it is difficult to decrease this intake, it has been suggested that the water intake should be as low as possible (Health and Welfare Canada 1980).

1.3.1.6.2 Canadian Exposure

The main source of cadmium intake is food. Total-diet studies have shown that people residing in the Ottawa-Hull, Halifax and Vancouver areas ingest an average of 0.08, 0.067 and 0.067 mg·d^{-1}, respectively. The overall range for Canadians is 0.05-0.098 mg·d^{-1} (Health and Welfare Canada 1980).

A survey on Canadian water supplies indicated median cadmium concentrations in raw and distributed river and lake waters to be less than or equal to 0.01 mg·L^{-1}. Maximum concentrations in raw and distributed waters were found to be 1.13 and 0.27 μg·L^{-1}, respectively (Méranger *et al.* 1979). At the maximum concentration of 0.27 μg·L^{-1}, the drinking water contribution at a 2 L·d^{-1} consumption would be much less than 1 μg·d^{-1}. There has been some indication in non-Canadian studies that cadmium concentrations can be increased through plumbing and distribution services within a waterworks (NAS 1977).

1.3.1.6.3 Water Treatment

Most water treatment performance assessments have been based on laboratory or pilot-scale evaluations. It has been found that coagulation can remove cadmium, but that pH is an important variable. Using alum, pH 9 was required for 90% removal although turbidity would assist cadmium removal with the aluminum salt (Sorg *et al.* 1978). Generally, alum coagulation removal of less than 30-60% cadmium may be appropriate. Iron salts were found to be more effective, probably because of their lesser dependence on pH. Ferric sulphate could remove from 60% to greater than 90% cadmium above pH 7.5 (NAS 1977). Although there is no test information available, use of alum for certain situations requiring low pH (e.g. colour removal) may in fact cause some dissolution of cadmium from sediment (Wiley and Nelson 1984).

Lime softening has been found to be quite effective for cadmium removal because of the high pH values encountered, and removals approaching 100% may be achieved. Special treatment for cadmium is not readily available. Activated carbon could provide low removals in the 10-50% range (Sorg *et al.* 1978).

1.3.1.7 Chloride

1.3.1.7.1 Existing Drinking Water Guideline

The Canadian maximum acceptable chloride concentration is 250 mg·L^{-1} (Health and Welfare Canada 1979a). The chloride anion, with its associated cations, contributes significantly to the osmotic activity of the extracellular fluid. Eighty-eight percent of the chloride in the body is extracellular and is important for bodily functions (Health and Welfare Canada 1980; NAS 1980a). Because water is a relatively minor contributor of chloride, health implications with respect to chloride in water are not significant. The main consideration regarding chloride is prevention of undesirable taste in water or water-based beverages (Health and Welfare Canada 1980). Some surface waters could be subject to significant seasonal chloride fluctuations, and this should be considered during source assessments.

1.3.1.7.2 Canadian Exposure

The total daily intake of chloride from food, water and air is estimated to be 6020 mg, but this could vary as a result of salt use in cooking and as a condiment. Only 20 mg·d^{-1} of this daily intake is likely to be the contribution from drinking water (Health and Welfare Canada 1980).

Available Canadian drinking water quality data indicate chloride concentrations are generally below 10 mg·L^{-1}, although individual supplies could have much greater concentrations depending on the nature of the source water (Health and Welfare Canada 1980).

1.3.1.7.3 Water Treatment

Because of its soluble and conservative or unreactive nature, chloride is not easily removed from water, and demineralization processes, such as reverse osmosis, ion exchange, distillation or separation by freezing, are required (American Water Works Association 1971; Baker 1981). These can be used to treat all or a portion of the raw water, depending on blending feasibility. Although technology is available to provide product waters with low chloride levels, the economic feasibility has to be carefully considered.

1.3.1.8 Chromium

1.3.1.8.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend that the maximum acceptable chromium concentration should not exceed 0.05 mg·L^{-1} (Health and Welfare Canada 1979a). Of the chromium species normally present in surface water, Cr(III) is essential to humans and animals, whereas Cr(VI) has adverse physiological effects (NAS 1977). Because trivalent chromium is unlikely to occur in waters above pH 5, hexavalent chromium in the form of either chromates or dichromates is of greater concern in water supplies because these compounds are quite soluble and mobile in the environment (U.S. EPA 1979). Cr(VI) is not considered to be an essential nutrient, and known harmful effects of chromium in humans are attributed to this form. At 0.05 mg·L^{-1}, hexavalent chromium has not caused any known harmful effects on the health of humans or other animals (Health and Welfare Canada 1980).

1.3.1.8.2 Canadian Exposure

The total daily intake of chromium from food, air and water has been estimated to be about 0.2 mg. Of this, the average dietary contribution, based on typical diets in three Canadian cities, is 0.189 mg·d^{-1}. The intake through water consumption is a minor fraction (Health and Welfare Canada 1980). A study on Canadian drinking water supplies found chromium concentrations of 2 µg·L^{-1} in raw surface waters and groundwaters (Méranger *et al.* 1979). Treated and distributed waters yielded the same median value, with overall ranges from less than 2 to 9 µg·L^{-1}. Consumption of 2 L·d^{-1} at the maximum level would provide only 0.018 mg·d^{-1} exposure to chromium.

1.3.1.8.3 Water Treatment

For water treatment, the valence state of chromium must be considered. Because of its high solubility, Cr(VI) is much more difficult to remove than Cr(III). Chlorination may convert Cr(III) to Cr(VI), which could create additional treatment problems. However, conventional treatment using iron salt or alum coagulants is reasonably effective for the removal of Cr(III), and removals can reach 90%, with iron coagulants being more effective than alum (Sorg 1979).

Treatment of Cr(VI) is very difficult with straight coagulation unless a reducing substance is used. Ferrous sulphate has been found to be a reasonably effective coagulant for removal of Cr(VI) in drinking water, as it converts Cr(VI) to Cr(III) (Sorg 1979). The use of ferrous sulphate is not universally practiced in Canada and this cannot be considered a common treatment approach.

Lime softening is effective for 80-90% removal of Cr(III); however, Cr(VI) is not readily controlled even at pH 9.5. Special treatment techniques are not readily available at this time for chromium removal, although reverse osmosis may be applicable (Sorg 1979).

1.3.1.9 Copper

1.3.1.9.1 Existing Drinking Water Guideline

Copper is considered to be a beneficial and essential element for humans, and is generally nontoxic (Health and Welfare Canada 1980). The 1.0 mg·L^{-1} Canadian maximum acceptable concentration is based on staining of laundry and plumbing fixtures. Other aesthetic considerations, such as unpleasant taste, occur above this concentration (Health and Welfare Canada 1979a).

1.3.1.9.2 Canadian Exposure

For Canadians, the total daily intake of copper has been estimated at 2.4 mg, with food contributing 2.2 mg·d^{-1} (Health and Welfare Canada 1980).

A survey of selected Canadian municipal water supplies found median copper concentrations of less than or equal to 5 µg·L^{-1} in raw and treated waters and 20-75 µg·L^{-1} in distributed waters (Méranger *et al.* 1979). The same study reported maximum copper concentrations in plant effluent and tap waters of 0.1 and 0.56 mg·L^{-1}, respectively, and observed that soft and corrosive supplies yielded the greater distribution system contributions. Increases in copper concentration in going from the plant to the tap have also been reported elsewhere, particularly for soft, nonalkaline waters; however, decreases because of precipitation and deposition within a distribution system have also been reported (NAS 1977, 1982; Karalekas *et al.* 1983).

1.3.1.9.3 Water Treatment

Treatment processes for control of copper concentrations could include techniques to remove copper from raw water or to minimize copper leaching from within a waterworks. Copper removal processes are not extensively documented. Aeration and/or upward pH adjustment decreases the solubility of copper, which would enhance coagulation and/or filtration removal mechanisms. Alum coagulation, based on laboratory-scale work, has been reported to effect removals in the 60-90% range (NAS 1977). Distribution system corrosion control measures, which have been used successfully, include pH adjustment with sodium hydroxide (Karalekas *et al.* 1983).

1.3.1.10 Cyanide

1.3.1.10.1 Existing Drinking Water Guideline

The maximum acceptable concentration of free cyanide of 0.2 mg·L^{-1} is suggested in the current Guidelines for Canadian Drinking Water Quality 1978 (Health and Welfare Canada 1979a). This is less than 10% of a noninjurious concentration at a 2 L·d^{-1} consumption rate (Health and Welfare Canada 1980).

1.3.1.10.2 Canadian Exposure

Although not quantified, Canadian exposure to cyanide is thought to be extremely low. Reported data on Canadian drinking water indicate low concentrations (<0.10 mg·L^{-1}) of cyanide (Health and Welfare Canada 1980).

1.3.1.10.3 Water Treatment

Little recent documentation on cyanide removal during drinking water treatment is available, perhaps because of an absence of need. In chlorination, chlorine gas or a hypochlorite reacts with free cyanide (hydrogen cyanide and cyanide ion) to form cyanate or effect complete destruction (White 1972; Leduc *et al.* 1982). An alkaline condition (pH 8.5-9.5) enhances the reaction and avoids the release of cyanogen chloride (White 1972; Pierce 1978). The effectiveness and dosages of chlorine will depend on other chlorine demands. Ozone is also particularly effective for cyanide oxidation (Rice *et al.* 1981). Singleton (1986) reported that chlorination of raw drinking water containing this cyanate can produce highly toxic cyanogen chloride (CNCl) which can persist for 24 h at pH 9 if no residual chlorine exists. Under acidic conditions, chlorination and ozonation of thiocyanate-contaminated water would favour the formation of HCN (hydrocyanic acid). High intensity ultraviolet light can photolyze thiocyanate to produce toxic HCN.

1.3.1.11 Fluoride

1.3.1.11.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 give a maximum acceptable concentration of 1.5 mg·L^{-1}. Fluoride has not been shown unequivocally to be an essential element for human nutrition, except for its effectiveness in reducing the incidence of dental caries (NAS 1980a). Fluoride concentrations in drinking water are primarily based on their effect on teeth, one of the most fluoride-sensitive tissues, and are set to avoid objectionable dental fluorosis (mottling) (NAS 1977; Health and Welfare Canada 1980).

1.3.1.11.2 Canadian Exposure

Estimated average daily intakes for Canadians from major (food and fluoridated drinking water) and minor (air and fluoridated dentifrices) fluoride sources have been reported as 2.7 mg for adults and less than 2 mg for children. Where the drinking water fluoride concentration is low, suggested intakes range from 0.3 to 0.5 mg·d^{-1} for persons over 12 years of age (Health and Welfare Canada 1980).

Fluoride concentrations in drinking water will vary, primarily because of the artificial fluoride additions that are practised at a number of Canadian waterworks. In some cases, natural levels exceed the normal fluoridation objective of 1 mg·L^{-1}. Concentrations of fluoride in natural water supplies in various parts of Canada range from less than 0.1 to 4.5 mg·L^{-1}. It is suspected that groundwater may be the source of most of these elevated fluoride concentrations (Health and Welfare Canada 1980).

1.3.1.11.3 Water Treatment

Fluoride-related water treatment involves the addition of fluoride through such chemicals as sodium fluoride, sodium silicofluoride or fluorosilicic acid, and the removal of fluoride from raw waters containing undesirable levels (American Water Works Association 1971).

Practical, effective water treatment processes for fluoride removal are both restricted and specialized. Conventional alum coagulation requires very high alum applications to obtain significant fluoride removals. It has been reported that 350 mg·L^{-1} alum was necessary to decrease concentrations of fluoride from 3.6 to 1 mg·L^{-1} (Sorg 1978). Lime softening may only be applicable for high magnesium waters with low fluoride concentrations, as high pH coprecipitation with magnesium hydroxide is necessary (Sorg 1978; Bishop and Sansoucy 1978).

Specialized treatment, particularly ion-exchange adsorption, is more favourable for fluoride removal. Bone char and activated alumina are the more successful media. Laboratory studies and full-scale operations have demonstrated the efficiency of activated alumina, with removals in excess of 90% or to less than 1 $mg{\cdot}L^{-1}$ from 5-8 $mg{\cdot}L^{-1}$ fluoride concentrations in raw water (Sorg 1978; Bishop and Sansoucy 1978; Choi and Chen 1979b). Reverse osmosis can also achieve significant fluoride removals. Fluoride data from operating reverse osmosis plants suggest removals to less than 1 from 2.2 $mg{\cdot}L^{-1}$ in raw waters (Naylor and Dague 1975).

1.3.1.12 Iron

1.3.1.12.1 Existing Drinking Water Guideline

Iron is an essential element in human nutrition, but food sources generally provide the minimum requirements. The maximum acceptable concentration in Canadian drinking water has been set at 0.3 $mg{\cdot}L^{-1}$ on the basis of aesthetic considerations (Health and Welfare Canada 1979a). The main effects of excessive iron include staining of laundry and plumbing, unpleasant taste, colour and the potential promotion of undesirable biological growths within a waterworks (Health and Welfare Canada 1980).

1.3.1.12.2 Canadian Exposure

With food the major contributor, it has been estimated that the daily iron intake for Canadian individuals is 18 mg (Health and Welfare Canada 1980).

Iron concentrations in drinking water can be quite variable, and depend on the source, treatment employed and inputs from distribution system corrosion. Canadian drinking waters generally contain less than 1.0 $mg{\cdot}L^{-1}$ of iron and often contain less than 0.3 $mg{\cdot}L^{-1}$ (Health and Welfare Canada 1980).

1.3.1.12.3 Water Treatment

Under aerobic conditions, much of the iron in surface waters will probably be in the insoluble form or attached to suspended particulates which are readily amenable to treatment. It is recognized that surface water impoundments under reducing conditions (e.g. ice cover) may be subject to seasonal soluble iron fluctuations. The iron in groundwaters would generally be in a soluble form (McDonald 1986).

The types of treatment processes used for the removal of iron from public water supplies vary with the form and concentration of iron in raw water, and with treatment requirements for other variables. Generally, removal techniques will involve precipitation step(s) followed by filtration. Sedimentation may be used prior to filtration. Formation of insoluble and filterable iron may be accomplished by aeration, chemical oxidation (chlorine, potassium permanganate, ozone), pH adjustment, lime precipitation, or passage through specially treated zeolites. Various granular media filtration techniques can be used for removal of insoluble iron. Ion exchange can also be employed (American Water Works Association 1971; Baker 1981).

In cases where iron removal requirements are marginal, sequestering of iron with sodium silicate or polyphosphate can be utilized to minimize aesthetic problems for consumers (American Water Works Association 1971; Dart 1983).

Removal of iron, especially from groundwater supplies, is relatively common. Proven treatment technology exists to satisfactorily reduce iron concentrations from the 5-10 $mg{\cdot}L^{-1}$ range to below 0.3 $mg{\cdot}L^{-1}$. Surface water treatment plants operated for turbidity removal would inherently remove much of the total iron in raw waters unless it was present as nonlabile organic complexes.

1.3.1.13 Lead

1.3.1.13.1 Existing Drinking Water Guideline

Lead is not considered to be an essential trace element. The maximum acceptable concentration of 0.05 $mg{\cdot}L^{-1}$ in the Guidelines for Canadian Drinking Water Quality 1978 (Health and Welfare Canada 1979a) maintains a total daily intake for nonoccupationally exposed adults of less than 3 mg per person per week (Health and Welfare Canada 1980).

1.3.1.13.2 Canadian Exposure

Estimates of daily exposure to lead from air, water and food vary. Air intakes ranging from an average of 14.8 $\mu g{\cdot}d^{-1}$ to a maximum of 64.4 $\mu g{\cdot}d^{-1}$, drinking water contributions of 16-18 $\mu g{\cdot}d^{-1}$, and a food intake of 0.13 $mg{\cdot}d^{-1}$ have been suggested. It has also been suggested that up to 0.3 mg may be ingested daily, with food being the major source (Health and Welfare Canada 1980).

Canadian tap water has been reported to contain an average of 7.6 $\mu g{\cdot}L^{-1}$ of lead (Health and Welfare Canada 1980). A survey at selected Canadian sites, using surface waters and groundwaters, found the median concentrations of lead in raw, treated and distributed water to be less than or equal to 1 $\mu g{\cdot}L^{-1}$ (Méranger *et al.* 1979). The maximum treated and distributed water concentrations were 95 and 23 $\mu g{\cdot}L^{-1}$, respectively. With soft water and periods of stagnation in pipe services or soldered connections, elevated lead concentrations can occur in tap water (Health and Welfare Canada 1980; NAS 1982).

1.3.1.13.3 Water Treatment

Although most of the performance evaluations are based on laboratory or pilot plant studies, it appears that conventional coagulation or lime softening can provide significant removal of lead. Alum coagulation was found to achieve removals of 60-80% at low pH (6.5-7), and greater than 90% at a high pH (>9.5) (NAS 1977; Sorg *et al.* 1978). Ferric sulphate was found to be more effective for lead removal from raw water with low turbidity and high lead concentrations (Sorg *et al.* 1978; U.S. EPA 1978b). Lime softening, at pH 9-11, was found capable of removing lead by over 90% (Naylor and Dague 1975; Sorg *et al.* 1978; NAS 1982). Special treatment techniques, such as ion exchange and reverse osmosis, could also potentially remove substantial amounts of lead (NAS 1977; Sorg *et al.* 1978).

1.3.1.14 Manganese

1.3.1.14.1 Existing Drinking Water Guideline

Manganese is an essential element in animals and man (NAS 1977; Health and Welfare Canada 1980). Concentrations related to possible health concerns are much greater than those related to aesthetic considerations, and therefore the latter have governed drinking water quality guidelines. Staining of plumbing and laundry, together with undesirable taste, occur at concentrations in excess of 0.15 mg·L^{-1}, and encrustation problems in piping may be encountered at a concentration of 0.02 mg·L^{-1}. The current Canadian maximum acceptable concentration of 0.05 mg·L^{-1} manganese in drinking water (Health and Welfare Canada 1979a) is based on the lowest level reasonably achievable with treatment (Health and Welfare Canada 1980).

1.3.1.14.2 Canadian Exposure

The total daily intake of manganese by Canadians from all environmental sources has been estimated to be just over 3.6 mg. In this estimate, food was considered to be the major contributor, with drinking water and air being only very minor sources (Health and Welfare Canada 1980).

Generally, reported concentrations of manganese in Canadian drinking waters are below 0.05 mg·L^{-1}. However, water supply values as high as 4.6 mg·L^{-1} have been recorded (Health and Welfare Canada 1980). Manganese may deposit in distribution systems and could be released in slugs (NAS 1982).

1.3.1.14.3 Water Treatment

Elevated manganese concentrations may occur in waters with high iron content, and thus treatment processes may be intended for joint control of the two substances. In general, manganese is more difficult to control than iron. Both removal and sequestering techniques have been employed.

For removal of manganese, conversion of soluble forms to insoluble precipitates followed by filtration is the general approach. Although manganese is difficult to oxidize, agents such as potassium permanganate, chlorine and ozone have been used. Insoluble manganese can be formed at high pH during lime softening (American Water Works Association 1971; Baker 1981). Removal efficiencies for coagulation with ferric sulphate at high pH ranged from 30 to 90%; for excess lime softening they ranged from 60 to 90% (NAS 1977). The use of special granular media such as manganese greensand for oxidation/ion exchange/filtration has generally been successful for many groundwater sources (American Water Works Association 1971).

1.3.1.15 Mercury

1.3.1.15.1 Existing Drinking Water Guideline

Mercury is a toxic element and serves no beneficial physiological function in humans (Health and Welfare Canada 1980). The maximum acceptable concentration of all forms of mercury in water, 1 µg·L^{-1} (Health and Welfare Canada 1979a), restricts the intake from drinking water to less than 10% of the tolerable level (Health and Welfare Canada 1980).

1.3.1.15.2 Canadian Exposure

The average daily mercury intake from air, food and water has been estimated to be less than 15 µg per person. Of this total, the Canadian daily intake from food, exclusive of diets high in fish and shellfish, has been considered to be 13 µg per person (Health and Welfare Canada 1980).

In natural waters, the concentrations of mercury in the water column are quite low, and these low concentrations are reflected in the limited data base on drinking water quality. Median concentrations of mercury in Canadian drinking water from three provinces have been reported to be 0.29 µg·L^{-1} or less (Health and Welfare Canada 1980).

1.3.1.15.3 Water Treatment

The capability and performance of water treatment processes depend on the form(s) of mercury present, the removal required and other raw water characteristics such as turbidity and substances that may bind mercury. Based on laboratory and pilot plant studies, conventional coagulation-filtration treatment using alum or ferric sulphate could remove up to 70-80% of inorganic mercury in turbid raw waters (Logsdon and Symons 1973; Sorg 1979). Very low turbidities substantially reduce removals to one-half or less. Organic mercury has been found to be not materially affected during coagulation processes (Logsdon and Symons 1973). Water softening using lime was also found to be ineffective for removal of organic mercury, but removals of the inorganic species range from 50 to 80% (Logsdon and Symons 1973; Sorg 1979).

Special treatment techniques, such as activated carbon adsorption, appear to be reasonably effective for removal of both inorganic and organic mercury, based on limited studies. Removals of about 90% appear to be achievable (Logsdon and Symons 1973; Sorg 1979; Huang and Blankenship 1984). For organic mercury, special treatment using activated carbon adsorption appears to be the only viable removal process.

1.3.1.16 Nitrate and Nitrite

1.3.1.16.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water 1978 recommend a maximum acceptable concentration of nitrate of 10 mg·L^{-1}. The maximum acceptable concentration of nitrite in drinking water is 1.0 mg·L^{-1}. Where nitrite is present, the sum of nitrogen in the form of nitrate and nitrite should not exceed 10 mg·L^{-1} (Health and Welfare Canada 1979a).

A high nitrate concentration in a drinking water supply is related to the occurrence of infantile methemoglobinemia, which results from the conversion of nitrate to nitrite. Most water-related cases of this have been associated with water containing more than 45 mg·L^{-1} nitrate (10 mg·L^{-1} NO_3–N) (Health and Welfare Canada 1980). Aside from health concerns, there are other implications in terms of public surface water supplies. For example, excessive nitrate concentrations could foster nuisance growths of aquatic organisms, such as algae. There is also the potential for seasonal variations in nitrate concentrations from the use of fertilizers.

1.3.1.16.2 Canadian Exposure

Food is the most significant source of nitrates for adults, but water plays a more important role for infants. Nitrates are a natural constituent of plant material, and occur at relatively high levels in vegetables. Cured meat contributes dietary nitrate to a lesser extent. The daily intake of nitrates for an adult Canadian has been estimated as 230 mg. Infant intake was estimated to be about half this amount (Health and Welfare Canada 1980). In comparison, the daily intake from water has been estimated to be approximately 9 mg for adults and 3 mg for infants (Health and Welfare Canada 1980).

Nitrite is rapidly oxidized to nitrate and is therefore seldom present in surface waters in significant concentrations. Nitrite may occur in groundwater sources, if chlorination is practised, it will be oxidized. The contribution of nitrite to the total daily intake of nitrate and nitrite should be negligible for most public water supplies. Food contributes more nitrite than does water to the Canadian diet (Health and Welfare Canada 1980).

The average daily intake of nitrite from food (including vegetables and cured meats) is approximately 11.6 mg for a Canadian adult and 3.9 mg for a Canadian infant. Because nitrites are oxidized to nitrates in chlorinated waters, nitrite intake from drinking water is negligible (Health and Welfare Canada 1980).

1.3.1.16.3 Water Treatment

Conventional water treatment is not effective for nitrate removal. Of the special treatment techniques that are available, only ion exchange has received substantial attention. In full-scale facilities for groundwater treatment, removals of 50% or more seem to be readily achievable using anion-exchange resins (Sorg 1978; Guter 1982).

Nitrite, normally not found in surface water but possible in groundwater, is rapidly oxidized to nitrate by chlorination (Health and Welfare Canada 1980).

1.3.1.17 pH

1.3.1.17.1 Existing Drinking Water Guideline

The acceptable range for drinking water pH of 6.5-8.5 as given in the current Canadian guidelines (Health and Welfare Canada 1979a) is primarily based on minimizing corrosion and encrustration, with consideration of the effectiveness of chlorine disinfection and formation of trihalomethanes (Health and Welfare Canada 1980).

1.3.1.17.2 Canadian Exposure

No data are available on pH ranges in Canadian drinking water. It has been reported that a U.S. survey determined a pH range from pH 5.0 to 10.5, with a median value of 7.5 (Health and Welfare Canada 1980). Compliance with current Canadian drinking water quality guidelines would provide a range of pH 6.5-8.5 (Health and Welfare Canada 1979a).

1.3.1.17.3 Water Treatment

Many water treatment processes affect and are affected by the pH of the source water. Common processes that can affect pH include gas chlorination, alum coagulation, aeration, lime-soda ash softening and recarbonation. Raw water pH may affect the performance and effectiveness of such processes as air stripping, chemical oxidation, chlorine disinfection, coagulation for turbidity and colour control and chemical softening (American Water Works Association 1971). Control procedures are technically available to either increase or decrease pH to desired levels. The feasibility and necessary operational rigour would depend on the temporal variability of the pH of the source water, its buffering capacity and other characteristics.

1.3.1.18 Selenium

1.3.1.18.1 Existing Drinking Water Guideline

Selenium is considered to be an essential nutrient for animals, but its role in human nutrition is unclear (Health and Welfare Canada 1980). Because of complex interrelationships between selenium and other dietary constituents, it is difficult to establish concentrations considered to be toxic. Therefore, the maximum acceptable concentration in drinking water is listed in the Guidelines for Canadian Drinking Water Quality 1978 as 0.01 $mg \cdot L^{-1}$ (Health and Welfare Canada 1979a). At this concentration, drinking water would contribute only 10% of the total selenium intake (Health and Welfare Canada 1980).

1.3.1.18.2 Canadian Exposure

The total daily intake of selenium from food, air and water has been estimated to be 0.2 mg per person. Of these sources, food has been suggested to contribute 0.17 $mg \cdot d^{-1}$ per person, with very small intakes from water and air (Health and Welfare Canada 1980).

Based on limited data, selenium concentrations in Canadian drinking water are low. One survey indicated most concentrations to be below 5 $\mu g \cdot L^{-1}$, with no concentrations above 10 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1980).

1.3.1.18.3 Water Treatment

The oxidation state of the primary selenium species, selenite (Se(IV)) or selenate (Se(VI)), influences the performance of water treatment processes. Based on laboratory and jar test studies, Se(IV) was decreased 40-80% by ferric sulphate coagulation and up to 50% by high pH lime softening (Sorg and Logsdon 1978). In the same studies, alum coagulation was found to be much less effective. Both types of conventional treatment removed only minor amounts (10%) of Se(VI).

Special treatment using fixed bed activated alumina adsorbers in bench- and pilot-scale applications was found capable of greater than 90% Se(IV) removal under pH constraints (decreased efficiency at pH 8 or greater), but significant Se(VI) removal required a very low pH (pH 4) (Hornung *et al.* 1983).

1.3.1.19 Silver

1.3.1.19.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 cite the maximum acceptable concentration of silver in drinking water as 0.05 $mg \cdot L^{-1}$ (Health and Welfare Canada 1979a). Silver is a nonessential element (Health and Welfare Canada 1980). The principal effect of silver intake by humans is argyria, a cosmetic condition characterized by a blue-gray discolouration of the eye, skin and mucous membranes (Health and Welfare Canada 1980; NAS 1982). The condition has been caused by a single injected dose of 1000 mg of silver as silver arsphenamine (Health and Welfare Canada 1980). Silver is only fractionally retained in the body (NAS 1977).

1.3.1.19.2 Canadian Exposure

Because of the limited amount of Canadian survey data on concentrations of silver in air, food and water, it has been suggested that a reliable estimate of daily exposure cannot be made (Health and Welfare Canada 1980). As the amount of dissolved silver in natural waters is quite low, exposure through consumption of water would be minimal; however, some vegetables are capable of concentrating silver during the cooking process (Health and Welfare Canada 1980; Hickman 1984).

Data on concentrations of silver in Canadian drinking water are not readily available (Health and Welfare Canada 1980).

1.3.1.19.3 Water Treatment

Because silver contamination of water supplies has not been a reported problem, treatment process evaluations have been limited and generally confined to laboratory and pilot plant studies. Surface waters containing significant turbidity (reported as 39 JTU) could lose 50% of the silver through sedimentation (U.S. EPA 1978b). Coagulation using alum or ferric chloride could cause silver removals in the 60-80% range, although the pH range for alum is somewhat narrow (Sorg *et al.* 1978). The same studies found that lime softening could produce slightly better removals (70-90%), depending on the pH attained. In addition to precipitation softening, groundwaters may be treated by ion exchange or reverse osmosis, but the practicality and efficiency of these special processes are not documented.

1.3.1.20 Sulphate

1.3.1.20.1 Existing Drinking Water Guideline

The Canadian maximum acceptable concentration for sulphate is 500 $mg{\cdot}L^{-1}$ (Health and Welfare Canada 1979a). The major concerns related to sulphate in drinking water are catharsis, gastrointestinal irritation and unpleasant taste. The current Canadian drinking water guideline is based on the potential for diarrhea in children consuming water with magnesium sulphate concentrations in excess of 600 $mg{\cdot}L^{-1}$. The taste threshold for sodium sulphate is 200-500 $mg{\cdot}L^{-1}$; it is higher for other sulphates (Health and Welfare Canada 1980). Some surface waters could be subject to significant seasonal variations in sulphate concentrations, and this should be considered during source evaluations.

1.3.1.20.2 Canadian Exposure

Canadian data on sulphate intake are not available, although U.S. intakes from food and air have been suggested to be 453 and 0.2 $mg{\cdot}d^{-1}$, respectively. Drinking water contributions have been estimated at less than 116 $mg{\cdot}d^{-1}$ for most Canadians, although some water supplies could provide more than 1000 $mg{\cdot}d^{-1}$ (Health and Welfare Canada 1980).

The sulphate concentration in drinking water can vary substantially across Canada, particularly where groundwater sources are used. For some provinces, the reported concentrations have ranged from less than 10 $mg{\cdot}L^{-1}$ to as high as 1795 $mg{\cdot}L^{-1}$ (Health and Welfare Canada 1980).

1.3.1.20.3 Water Treatment

Because of the high solubility of most sulphate salts, sulphate is not removed through conventional treatment processes. Where aluminum or iron sulphate coagulants are used, minor amounts may be added.

Desalination techniques, such as ion exchange, reverse osmosis, electrodialysis and separation by freezing, are required for sulphate removal. These can be employed to treat all or a portion of the water depending on the blending feasibility with respect to sulphate or other dissolved constituents. Without economic and operating constraints, treatment technology is available to remove substantial amounts of sulphate (American Water Works Association 1971; Baker 1981).

1.3.1.21 Sulphide

1.3.1.21.1 Existing Drinking Water Guideline

The most sensitive effects of sulphides and hydrogen sulphide in drinking water are disagreeable taste and odours. Because of the low taste and odour threshold, the Canadian maximum acceptable concentration of sulphide (as hydrogen sulphide) has been set at 0.05 $mg{\cdot}L^{-1}$ (Health and Welfare Canada 1979a).

1.3.1.21.2 Canadian Exposure

Daily dietary intakes of sulphide by Canadians are not available. Natural sulphide concentrations in air would result in daily intakes of 3-10 μg (Health and Welfare Canada 1980).

Sulphide concentrations in drinking water supplies are not documented (Health and Welfare Canada 1980).

1.3.1.21.3 Water Treatment

Measures for sulphide control, which depend on the species present and the causal factors, could be undertaken at the raw water source or in the treatment process train; measures preventing its generation within the distribution system could also be undertaken.

Source treatment includes the use of aeration to oxidize sulphide or, more importantly, expel dissolved hydrogen sulphide through volatilization. Aeration may also be used to prevent ice cover and thereby minimize generation factors or decrease the concentration of sulphide.

Treatment plant processes for sulphide removal include aeration, metal precipitation and chemical oxidation. Potential chemical oxidants include chlorine, potassium permanganate, ozone and ferrate. Hydrogen sulphide removals to less than 0.05 $mg{\cdot}L^{-1}$ are reasonably achievable (Prakash 1976). Maintenance of suitable oxidizing conditions and prevention of sulphate-reducing bacterial growths can mitigate internal system generation of sulphides.

1.3.1.22 Total Dissolved Solids

1.3.1.22.1 Existing Drinking Water Guideline

The Canadian maximum acceptable concentration guideline of 500 $mg{\cdot}L^{-1}$ is based primarily on aesthetic (palatability) considerations (Health and Welfare Canada 1979a). Excessive concentrations can also effect corrosion or encrustration within a waterworks(Health and Welfare Canada 1980).

1.3.1.22.2 Canadian Exposure

Concentrations of total dissolved solids in Canadian drinking water are not well documented. Reported concentrations in five provinces ranged from 20 to 3800 mg·L^{-1}, which reflects the variations in surface water and groundwater quality across Canada (Health and Welfare Canada 1980). It is expected that some supplies, particularly surface waters, have considerable seasonal variations in concentrations of total dissolved solids. The lack of optional sources may force some use of waters with higher-than-desired concentrations of total dissolved solids.

1.3.1.22.3 Water Treatment

Because total dissolved solids include the soluble ions of bicarbonate, chloride, sulphate, calcium, magnesium, sodium and potassium, treatment for removal reflects processes for the removal of the individual constituents and the interrelated groupings. Certain treatment processes, such as lime-soda ash softening and sodium exchange zeolite softening, may cause minor decreases or increases, respectively.

To effectively remove total dissolved solids, a desalination process, such as reverse osmosis, distillation or separation by freezing, is required. The technology is available to produce the desired water quality, but the economic feasibility may be a major constraint (American Water Works Association 1971; Baker 1981).

1.3.1.23 Uranium

1.3.1.23.1 Existing Drinking Water Guideline

The maximum acceptable concentration of 20 µg·L^{-1} established in the current Canadian drinking water guidelines, which use chemical toxicity as the factor to be considered (Health and Welfare Canada 1979a), provides a drinking water allowance of about 50% of the no-effect-level intake (U.S. EPA 1978b). Uranium is not considered to be essential for humans (Health and Welfare Canada 1980).

The 1978 guideline is being updated, taking recent studies into account. The final analyses will not be completed in time to include them in this edition. The Canadian drinking water guidelines can be adapted to local water conditions, thus local guidelines could be different from those found in the Canadian Drinking Water Guidelines 1978.

1.3.1.23.2 Canadian Exposure

Accurate Canadian data on uranium intake are lacking, but estimates suggest total daily intake to be less than 3 µg, with food contributing about 1.4 µg·d^{-1}. Drinking water data from a number of Canadian cities, based on monthly composite samples, indicate normal concentrations are less than 1 µg·L^{-1}, with a recorded maximum of 6 µg·L^{-1} (Health and Welfare Canada 1980).

1.3.1.23.3 Water Treatment

Studies on uranium removal by drinking water treatment are limited. A survey of selected existing treatment facilities in the United States was undertaken to determine uranium changes at significant treatment process points (White and Bondietti 1983). General findings suggested that coagulation (alum, iron salts, lime and/or polymers) and pH changes were ineffective for uranium removal from raw waters containing up to 15.9 µg·L^{-1} uranium. Further bench-scale studies found that lime and magnesium carbonate additions could effect substantial uranium removals under optimum pH and magnesium conditions. In the same work, coagulation was found to be reasonably effective at critical pH values. Special ion-exchange treatment using a strong-base anion resin was also successfully tested with 99% removals at a concentration of 83 µg·L^{-1}, and thus may have practical, small-scale applications (Lee and Bondietti 1983).

1.3.1.24 Zinc

1.3.1.24.1 Existing Drinking Water Guideline

The current Canadian maximum acceptable concentration of 5.0 mg·L^{-1} (Health and Welfare Canada 1979a) is based on aesthetic considerations (Health and Welfare Canada 1980). Zinc is considered to be an essential element for human nutrition (Health and Welfare Canada 1980; NAS 1980a). Aesthetic problems, such as undesirable taste and appearance, develop at concentrations below those related to any health concerns.

1.3.1.24.2 Canadian Exposure

Food, which is considered to be the largest dietary source of zinc, has been estimated to contribute from 15.2 to 19.9 mg·d^{-1} in a representative Canadian diet (Health and Welfare Canada 1980). Average intakes from drinking water have been estimated at 0.4 mg·d^{-1} (Health and Welfare Canada 1980) and less than or equal to 65 µg·d^{-1} (Méranger *et al*. 1979). Intakes from inhalation appear to be negligible (Health and Welfare Canada 1980).

Limited data on zinc concentrations in Canadian drinking water suggest that concentrations are generally less than 0.2 mg·L^{-1}, although values approaching 2 mg·L^{-1} have been observed (Health and Welfare Canada 1980). Another survey found median values of less than or equal to 5 µg·L^{-1} in raw, treated and distributed waters from surface water and groundwater sources (Méranger *et al*. 1979). The maximum concentration in distributed water was 0.2 mg·L^{-1}.

Increases in zinc concentration within distribution systems as a result of leaching or corrosion of galvanized pipes or brass fittings have been reported in Canadian and U.S. waterworks (Méranger *et al*. 1979; Health and Welfare Canada 1980; NAS 1982). Compounds of zinc may also be added for corrosion protection (NAS 1982), although no information is available on the prevalence of this practice in Canada.

1.3.1.24.3 Water Treatment

Few data are available on the performance of treatment processes for removal of zinc. Based on wastewater studies, alum coagulation at pH 6.5-7 has been reported to provide less than 30% removal, whereas lime softening at pH 9.5-10 provides 60-90% removal (NAS 1977). A survey of Canadian waterworks found that zinc concentrations in treated water could be higher or lower than concentrations in raw water (Méranger *et al.* 1979). It is expected that the success of zinc removal would depend on its form, binding to particulate matter and the pH regime of the treatment process. Soft water of low pH would probably impede removal of zinc. Zinc removal is generally ancillary or incidental to other treatment objectives.

1.3.2 Organic Parameters

1.3.2.1 Aldrin*

1.3.2.1.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 list the maximum acceptable concentration of aldrin plus dieldrin in drinking water as 0.7 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1979a). The acceptable daily intake (ADI) of aldrin and its transformation product, dieldrin, has been given as 0.1 $\mu g \cdot kg^{-1} \cdot d^{-1}$. The guideline is based on a 20% drinking water allowance of the ADI for a 70-kg person consuming 2 $L \cdot d^{-1}$ (Health and Welfare Canada 1980).

1.3.2.1.2 Canadian Exposure

The reported dietary intake of aldrin and dieldrin combined in selected Canadian cities ranged from 1 to 4 $\mu g \cdot d^{-1}$ per person (Health and Welfare Canada 1980).

Although available Canadian drinking water measurements are few, the reported concentrations have been in the 0.7-6.0 $ng \cdot L^{-1}$ range (Health and Welfare Canada 1980).

1.3.2.1.3 Water Treatment

Little information is readily available on the effect of water treatment on aldrin. Because of the chemical's characteristics, removal by aeration is probably minimal (Kavanaugh and Trussell 1980). Coagulation effectiveness of only about 10% has been reported (Edzwald *et al.* 1979). Special treatment processes such as ozonation or granular activated carbon adsorption are potentially effective processes, although performance data are lacking (Gomella 1972; NAS 1980b; Dobbs and Cohen 1980).

1.3.2.2 Chlordane

1.3.2.2.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend that the maximum acceptable concentration for all isomers of chlordane be 7 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1979a). This is based on a 20% allowance of the acceptable daily intake (1.0 $\mu g \cdot kg^{-1} \cdot d^{-1}$) for a 70-kg person ingesting 2 L of drinking water daily (Health and Welfare Canada 1980).

1.3.2.2.2 Canadian Exposure

Very limited drinking water data for two Canadian urban centres show concentrations of 0.05 and 5 $ng \cdot L^{-1}$ (Health and Welfare Canada 1980).

1.3.2.2.3 Water Treatment

Little information is readily available on conventional water treatment performance for chlordane removal. If chlordane is reduced in similar fashion to other cyclodienes, such as dieldrin and endrin, coagulation and filtration could yield 35-55% removals. Activated carbon adsorption characteristics for chlordane appear to be favourable (NAS 1980a; Dobbs and Cohen 1980), but treatment application data are lacking.

Chlordane has a low odour threshold (0.5 $\mu g \cdot L^{-1}$) (Sigworth 1965), which could influence treatment requirements.

1.3.2.3 2,4-D

1.3.2.3.1 Existing Drinking Water Guideline

The current Guidelines for Canadian Drinking Water Quality 1978 list the maximum acceptable concentration of 2,4-D as 0.1 $mg \cdot L^{-1}$ (Health and Welfare Canada 1979a). This was derived using 20% of an acceptable daily intake (Health and Welfare Canada 1980).

1.3.2.3.2 Canadian Exposure

There are no published measurements of 2,4-D in Canadian public waterworks (Health and Welfare Canada 1980).

1.3.2.3.3 Water Treatment

Conventional water treatment processes have been found to be ineffective for removal of 2,4-D at high concentrations (U.S. EPA 1978a). Chlorination of waters containing 2,4-D may accentuate organoleptic problems (McDonald 1986).

The only feasible treatment process readily available appears to be adsorption on activated carbon. The use of powdered activated carbon has been found effective for decreasing the sodium salt and ester 2,4-D formulations from 1.0 to 0.1 $mg \cdot L^{-1}$ using concentrations of activated carbon of 31 and 14 $mg \cdot L^{-1}$, respectively (U.S. EPA 1978a).

1.3.2.4 DDT

1.3.2.4.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 provide a maximum acceptable concentration of 0.03 $mg \cdot L^{-1}$ for total DDT isomers (Health and Welfare Canada 1979a). This value was derived from a 20% allowance of the acceptable daily intake (5.0 $\mu g \cdot kg^{-1} \cdot d^{-1}$) for a 70-kg person and a 2 $L \cdot d^{-1}$ water consumption (Health and Welfare Canada 1980).

1.3.2.4.2 Canadian Exposure

Analyses of food from selected Canadian cities between 1969 and 1973 indicated that daily dietary intakes of all isomers of DDT ranged from 7 to 18 μg per person (Health and Welfare Canada 1980).

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* See also Section 1.3.2.6.

A concentration of 0.05 $ng \cdot L^{-1}$ of all DDT isomers was found in an Ottawa tap water sample (Health and Welfare Canada 1980).

1.3.2.4.3 Water Treatment

Although conventional oxidation is relatively ineffective, chemical coagulation with alum or ferric salts and filtration have been reported to achieve DDT removals between 30 and 98% (Robeck *et al.* 1965; Edzwald *et al.* 1979). The sorption of DDT onto particulate matter may affect the efficiencies of the clarification processes. Considering reliability and the lack of full-scale plant operating data, conventional treatment removals of about 25% may be appropriate as a conservative estimate (McDonald 1986).

Although performance data are minimal, the adsorption characteristics for granular activated carbon appear to favour removals of DDT to a concentration of 1.0 $\mu g \cdot L^{-1}$ (Sigworth 1965; NAS 1980b; Dobbs and Cohen 1980).

1.3.2.5 Diazinon

1.3.2.5.1 Existing Drinking Water Guideline

The acceptable daily intake of diazinon is given as 2 $\mu g \cdot kg^{-1} \cdot d^{-1}$. The Guidelines for Canadian Drinking Water Quality 1978 indicate a maximum acceptable concentration of 14 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1979a). This is based on 20% of the ADI for a 70-kg person consuming 2 L of water daily (Health and Welfare Canada 1980).

1.3.2.5.2 Canadian Exposure

Dietary intakes of diazinon alone are not readily available. Grouped organophosphate pesticide intakes from foods in selected Canadian cities ranged from 1.0 to 5.0 $\mu g \cdot d^{-1}$ per person (Health and Welfare Canada 1980).

1.3.2.5.3 Water Treatment

Information on diazinon removal during drinking water treatment is not readily available. Other organophosphate pesticides (malathion and parathion) are ineffectively removed by coagulation (Edzwald *et al.* 1979). Similarly, these organophosphates are reported to be only moderately adsorbed (up to 50% removal) at low concentrations (0.05-0.1 $\mu g \cdot L^{-1}$) on granular activated carbon (van Lier *et al.* 1983).

1.3.2.6 Dieldrin*

1.3.2.6.1 Existing Drinking Water Guideline

Dieldrin, in combination with aldrin, has an acceptable daily intake value of 0.1 $\mu g \cdot kg^{-1}$ (Health and Welfare Canada 1980). The Guidelines for Canadian Drinking Water Quality 1978 suggest the maximum acceptable concentration of dieldrin plus aldrin in drinking water to be 0.7 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1979a). This concentration is based on a 20% allowance of the acceptable daily intake for a 70-kg person and a 2 $L \cdot d^{-1}$ water consumption (Health and Welfare Canada 1980).

1.3.2.6.2 Canadian Exposure

The reported dietary intake for both dieldrin and aldrin from food in selected Canadian cities ranged from 1 to 4 $\mu g \cdot d^{-1}$ per person (Health and Welfare Canada 1980).

Although available measurements of dieldrin and aldrin in Canadian drinking water are limited, reported concentrations are in the 0.05-5.0 $ng \cdot L^{-1}$ range (Health and Welfare Canada 1980).

1.3.2.6.3 Water Treatment

Little information is available on the removal of dieldrin through water treatment processes. Dieldrin, which has a very low Henry's law constant, has unfavourable air/water partitioning characteristics; therefore, aeration would probably be limited (Kavanaugh and Trussell 1980; Hess *et al.* 1983). The performance of the coagulation process has been poor, with reported removals of 10-50% using alum in water with low dieldrin concentrations (Edzwald *et al.* 1979).

Specialized treatment using activated carbon adsorption could probably be effectively employed. The adsorption characteristics for dieldrin are good (NAS 1980b; Dobbs and Cohen 1980). Results from pilot-scale granular activated carbon column studies indicate removals of better than 90% for dieldrin at concentrations as high as 4.3 $\mu g \cdot L^{-1}$ (McCreary and Snoeyink 1977).

1.3.2.7 Endrin

1.3.2.7.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend 0.2 $\mu g \cdot L^{-1}$ of endrin as the maximum acceptable concentration (Health and Welfare Canada 1979a). This is slightly below a 20% allowance of the acceptable daily intake (0.04 $\mu g \cdot kg^{-1} \cdot d^{-1}$) for consumption of 2 $L \cdot d^{-1}$ of drinking water by a 70-kg person (Health and Welfare Canada 1980).

1.3.2.7.2 Canadian Exposure

Endrin concentrations in drinking water in eastern Canada ranged from 0.05 to 7.0 $ng \cdot L^{-1}$ (Health and Welfare Canada 1980).

1.3.2.7.3 Water Treatment

The performance of conventional water treatment processes for the removal of endrin would be similar to that for the removal of other cyclodienes. Coagulation-filtration removals of 35% have been reported for waters containing 1 and 10 $\mu g \cdot L^{-1}$ of endrin (Robeck *et al.* 1965). However, others suggest the process to be relatively ineffective (U.S. EPA 1978b; Edzwald *et al.* 1979).

Activated carbon adsorption has potential for endrin removal. The adsorption capacity of granular activated carbon and the equilibrium concentration range appear favourable (NAS 1980b; Dobbs and Cohen 1980). Removals to 0.1 $\mu g \cdot L^{-1}$ have been observed in carbon adsorption tests using spiked river water (Robeck *et al.* 1965).

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* See also Section 1.3.2.1.

1.3.2.8 Heptachlor

1.3.2.8.1 Existing Drinking Water Guideline

Heptachlor and heptachlor epoxide (see Section 1.3.2.9) are considered jointly for drinking water purposes. The Guidelines for Canadian Drinking Water Quality 1978 indicate a maximum acceptable concentration of 3 $\mu g \cdot L^{-1}$ for the sum of these chlorinated hydrocarbons (Health and Welfare Canada 1979a). This concentration is based on an allowance of 20% of the acceptable daily intake (0.5 $\mu g \cdot kg^{-1} \cdot d^{-1}$) through the ingestion of 2 $L \cdot d^{-1}$ of drinking water by a 70-kg person (Health and Welfare Canada 1980).

1.3.2.8.2 Canadian Exposure

Analysis of Canadian municipal drinking water from two communities showed heptachlor concentrations ranging from 0.05 $ng \cdot L^{-1}$ to 5.0 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1980).

1.3.2.8.3 Water Treatment

Little information is available on the removal of heptachlor by conventional water treatment processes. Heptachlor may be amenable to loss through aeration. The performance of coagulation-filtration processes could be relatively ineffective, similar to that found for the removal of other cyclodienes (McDonald 1986).

Granular activated carbon has a very high adsorption capacity for heptachlor (NAS 1980b; Dobbs and Cohen 1980). No data are available to confirm the viability of this special treatment process.

1.3.2.9 Heptachlor Epoxide

1.3.2.9.1 Existing Drinking Water Guideline

Heptachlor epoxide, the principal metabolite of heptachlor, and heptachlor (see Section 1.3.2.8) are considered jointly for drinking water purposes. The Guidelines for Canadian Drinking Water Quality 1978 indicate a maximum acceptable concentration of 3.0 $\mu g \cdot L^{-1}$ for both chlorinated hydrocarbons (Health and Welfare Canada 1979a). This concentration is based on an allowance of 20% of the acceptable daily intake (0.5 $\mu g \cdot kg^{-1} \cdot d^{-1}$) through the ingestion of 2 $L \cdot d^{-1}$ of drinking water by a 70-kg person (Health and Welfare Canada 1980).

1.3.2.9.2 Canadian Exposure

At one Canadian urban location, the heptachlor epoxide concentration in drinking water was 0.05 $ng \cdot L^{-1}$ (Health and Welfare Canada 1980). Additional data are not readily available.

1.3.2.9.3 Water Treatment

The performance of conventional water treatment processes for the removal of heptachlor epoxide is not readily known. Presumably, coagulation-filtration would yield ineffective removals, similar to its capability with other cyclodienes (McDonald 1986).

Granular activated carbon has a very high adsorption capacity for heptachlor epoxide (Dobbs and Cohen 1980). No data are available to confirm whether adsorption would be as effective as anticipated.

1.3.2.10 Hexachlorocyclohexane (Lindane)

1.3.2.10.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend that the maximum acceptable concentration of lindane (the γ isomer of hexachlorocyclohexane) in drinking water should be 4 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1979a). The guideline is based on an acceptable daily intake level of 6 $\mu g \cdot kg^{-1} \cdot d^{-1}$ lindane by the average man weighing 70 kg. A 20% water source allowance yields an acceptable water concentration of 4.2 $\mu g \cdot L^{-1}$ for a 2 $L \cdot d^{-1}$ consumption rate (Health and Welfare Canada 1980).

1.3.2.10.2 Canadian Exposure

Very few data are available on measurements of lindane in drinking water. Those reported (from two cities) are quite low, ranging from 0.4 to 11 $ng \cdot L^{-1}$ (Health and Welfare Canada 1980).

1.3.2.10.3 Water Treatment

Water treatment performance has essentially been reviewed in terms of laboratory or pilot plant testing. Conventional surface water treatment processes have been relatively ineffective for lindane removal (U.S. EPA 1978a). The most favourable treatment process is adsorption on activated carbon. Lindane removals have been relatively effective using both powdered and granular activated carbon as a supplement to conventional treatment, with removals in the 80-90% range depending on the dosage and type of carbon and the lindane concentration (U.S. EPA 1978a; Wood and DeMarco 1979).

1.3.2.11 Methoxychlor

1.3.2.11.1 Existing Drinking Water Guideline

The Guidelines for Canadian Drinking Water Quality 1978 recommend the maximum acceptable concentration of methoxychlor to be 0.1 $mg \cdot L^{-1}$ (Health and Welfare Canada 1979a). This value is based on a 20% allowance of the acceptable daily intake (0.02 $mg \cdot kg^{-1} \cdot d^{-1}$) for a 70-kg person consuming 2 L of water daily (Health and Welfare Canada 1980).

1.3.2.11.2 Canadian Exposure

Only one measurement of methoxychlor in Canadian drinking water supplies, 0.05 $\mu g \cdot L^{-1}$, is available (Health and Welfare Canada 1980).

1.3.2.11.3 Water Treatment

The assessment of treatment process performance for methoxychlor removal is primarily based on bench-scale studies. Coagulation using alum or ferric sulphate was reasonably effective for water containing 1-10 $mg \cdot L^{-1}$ methoxychlor, with removals ranging from 73 to 93%; however, the residual concentration was in excess of 0.15 $mg \cdot L^{-1}$. Lime soda softening effected removals of 48-97%, but again residual concentrations exceeded 0.15 $mg \cdot L^{-1}$ (Steiner and Singley 1979).

Granular activated carbon adsorption was found to be quite effective on a laboratory-scale basis, with 1-10 mg·L^{-1} methoxychlor removal to less than 0.01 mg·L^{-1} (Steiner and Singley 1979).

1.3.2.12 Methyl Parathion

1.3.2.12.1 Existing Drinking Water Guideline

The maximum acceptable concentration of methyl parathion contained in the Guidelines for Canadian Drinking Water Quality 1978 is 7 μg·L^{-1} (Health and Welfare Canada 1979a). This value was derived from an acceptable daily intake of 1 μg·kg^{-1}·d^{-1} using a 20% allowance for ingestion of 2 L of drinking water daily by a 70-kg person (Health and Welfare Canada 1980).

1.3.2.12.2 Canadian Exposure

Data on Canadian exposure to this specific organophosphorus pesticide are not readily available. Surveys of food in selected Canadian cities for the organophosphate pesticide group indicated dietary intakes ranging from 1 to 5 μg·d^{-1} per person (Health and Welfare Canada 1980).

1.3.2.12.3 Water Treatment

Information on treatment capability and performance for removal of methyl parathion from water is not readily available. Treatment effectiveness may be similar to that for parathion removal.

1.3.2.13 Nitrilotriacetic Acid (NTA)

1.3.2.13.1 Existing Drinking Water Guideline

Nitrilotriacetic acid is poorly absorbed by humans and health implications of NTA are considered to be negligible (Health and Welfare Canada 1980). The current Canadian maximum acceptable concentration of 0.05 mg·L^{-1} in drinking water was based on a risk assessment which determined that there was a negligible risk of cancer (Health and Welfare Canada 1979a).

1.3.2.13.2 Canadian Exposure

The average daily intake of NTA by Canadians has been suggested to be 5.6 μg based on water as the sole source (Health and Welfare Canada 1980). This assumes an average concentration of NTA in drinking water of 2.8 μg·L^{-1}, which was obtained from a study that found a range of 0.2-30.4 μg·L^{-1} NTA in finished drinking water (Malaiyandi *et al.* 1979).

1.3.2.13.3 Water Treatment

Detailed process evaluation studies for NTA removal during water treatment are not generally available. Sewage treatment studies suggest that NTA is biodegradable but not readily adsorbed to solids and therefore not amenable to settling (Rudd and Hamilton 1972; Prakash 1976; Matheson 1977). Oxidation, considered to be a potentially effective treatment process, was examined on a laboratory scale using chlorine, chlorine dioxide and ozone (Hrubec *et al.* 1984). The chlorine disinfectants, at amounts used in water treatment, caused only slight degradation, whereas ozone, in excess of 4 mg·L^{-1}, provided nearly complete destruction. There are some suggestions that activated carbon will adsorb NTA (Prakash 1976).

Examination of data on concentrations of NTA in raw and treated water in many Canadian centres suggests that significant NTA removal does not occur even though a reasonable spectrum of treatment processes was used (Malaiyandi *et al.* 1979). This is consistent with observations that usual purification processes are not likely to remove NTA in appreciable amounts (Prakash 1976). Formation of undesirable products through NTA chlorination has not been demonstrated (Hrubec *et al.* 1984).

1.3.2.14 Parathion

1.3.2.14.1 Existing Drinking Water Guideline

The maximum acceptable concentration of parathion listed in the Guidelines for Canadian Drinking Water Quality 1978 is 35 μg·L^{-1} (Health and Welfare Canada 1979a). This value was apparently derived from an acceptable daily intake of 0.5 μg·kg^{-1}·d^{-1} and a 20% allowance for ingestion of 2 L of drinking water daily by a 70-kg person (Health and Welfare Canada 1980).

1.3.2.14.2 Canadian Exposure

Data on Canadian exposure to this specific organophosphorus pesticide are not readily available. Surveys of food in selected Canadian cities for the organophosphate pesticide group indicated dietary intakes ranging from 1 to 5 μg·d^{-1} per person (Health and Welfare Canada 1980).

1.3.2.14.3 Water Treatment

Pilot-scale testing for parathion removal examined chemical oxidation, coagulation-filtration, softening and activated carbon adsorption. The parathion concentrations used were approximately 10 μg·L^{-1}. High chlorine dosages were effective, but concerns may arise because of paraoxon formation. Removals by coagulation-filtration and softening were only in the 20 and 10% range, respectively (Robeck *et al.* 1965).

Granular activated carbon adsorption yielded 90% removal of parathion, but parathion may be competitively displaced if other chlorinated hydrocarbons are present. Experience in the Netherlands indicates moderate adsorption (20-50%) of organophosphate pesticides at relatively low concentrations (van Lier *et al.* 1983).

1.3.2.15 Phenols

1.3.2.15.1 Existing Drinking Water Guideline

Although phenolic compounds and halogenated phenol derivatives are toxic to man at high concentrations, taste and odour thresholds occur at much lower concentrations, and therefore aesthetic quality considerations prevail. The Canadian maximum acceptable concentration for phenols in drinking water is 2 μg·L^{-1} (Health and Welfare Canada 1979a). Unacceptable taste and odour are generated by phenol chlorination above concentrations of 5 μg·L^{-1} phenol (Health and Welfare Canada 1980).

1.3.2.15.2 Canadian Exposure

The total Canadian daily intake of phenol from air, food and drinking water has been estimated to be about 9 mg. Of this, the drinking water contribution is considered to be only 2 $\mu g{\cdot}d^{-1}$. Environmental sources appear to contribute substantially less phenols than the amount produced in the gastrointestinal tract (Health and Welfare Canada 1980).

Concentrations of phenols in Canadian drinking water are not well documented. One Ontario supply has been reported to contain up to 2 $\mu g{\cdot}L^{-1}$ (Health and Welfare Canada 1980).

1.3.2.15.3 Water Treatment

The treatment of water for removal of phenol will depend on the presence and type of phenolic compounds. In terms of simple phenols, potential drinking water treatment processes include oxidation and adsorption. Phenol removal through conventional iron or aluminum salt coagulation is probably 10% or less (Semmens and Ayers 1985).

Chemicals used for oxidation include chlorine, chlorine dioxide and ozone (American Water Works Association 1971). Chlorine oxidation using hypochlorous acid is difficult, because chlorophenols can be formed. These have more sensitive organoleptic thresholds thus magnifying the undesirable taste and odour characteristics (Lee 1967). Superchlorination may be necessary to ensure complete oxidation. Chlorine dioxide and ozone can be reasonably effective (American Water Works Association/American Society of Civil Engineers/Conference of State Sanitary Engineers 1971; NAS 1980b) but require special treatment applications.

Adsorption by activated carbon is also a potential treatment process. At low phenol concentrations (10 $\mu g{\cdot}L^{-1}$), the carbon requirement is reasonably feasible (18 $mg{\cdot}L^{-1}$ powdered activated carbon to decrease concentrations to 1 $\mu g{\cdot}L^{-1}$) (Dobbs and Cohen 1980).

1.3.2.16 2,4,5-TP

1.3.2.16.1 Existing Drinking Water Guideline

In the Guidelines for Canadian Drinking Water Quality 1978, the maximum acceptable concentration of 2,4,5-TP (fenoprop) is 0.01 $mg{\cdot}L^{-1}$ (Health and Welfare Canada 1979a). This is based on a 20% allowance of the acceptable daily intake (0.002 $mg{\cdot}kg^{-1}{\cdot}d^{-1}$) for a 70-kg person consuming 2 L daily (Health and Welfare Canada 1980).

1.3.2.16.2 Canadian Exposure

No data are available on intake of 2,4,5-TP by Canadians from air, food or drinking water.

1.3.2.16.3 Water Treatment

Data on drinking water treatment for 2,4,5-TP removal are not readily available. Limited pilot-scale studies on 2,4,5-T found chlorination to effect less than 10% removal, and coagulation plus filtration treatment removed about 63% from waters containing 0.01 $mg{\cdot}L^{-1}$ (Robeck *et al.* 1965). The same studies determined a 90% removal of 2,4,5-T using activated carbon adsorption. The similarity of response for 2,4,5-TP is not documented. It is suspected that the form and concentration in raw water could be important. The compound could also possess aesthetic properties detrimental to potable water supplies.

1.3.2.17 Toxaphene

1.3.2.17.1 Existing Drinking Water Guideline

Calculations used in supporting documentation for the Guidelines for Canadian Drinking Water Quality 1978 indicate a maximum acceptable limit of 8.8 $\mu g{\cdot}L^{-1}$, slightly greater than the reported 5.2 $\mu g{\cdot}L^{-1}$ threshold odour concentration (Health and Welfare Canada 1980). Thus, the current maximum acceptable concentration has been set at 5.0 $\mu g{\cdot}L^{-1}$ for organoleptic or aesthetic considerations (Health and Welfare Canada 1979a).

1.3.2.17.2 Canadian Exposure

Exposure of Canadians to toxaphene is apparently minimal, as toxaphene has been detected in only 0.6% of food samples from Canadian cities and has not been found in drinking water supplies. No quantitative intake data are available (Health and Welfare Canada 1980).

1.3.2.17.3 Water Treatment

Little published information is available on the performance of water treatment processes for the removal of toxaphene or any of the components that make up this mixture, perhaps because of the low incidence of occurrence or perceived needs. Toxaphene that is adsorbed onto settleable or suspended particulate matter may be partially removed by sedimentation or filtration, although no quantitative information is available (Guyer *et al.* 1971). Coagulation-filtration of toxaphene (probably soluble) has been reported to be ineffective (less than 10% removal). Treatment using chlorine or chlorine dioxide has also been noted as ineffective (U.S. EPA 1978a).

Adsorption by activated carbon appears to be a feasible treatment process, based on limited testing with powdered activated carbon (93% removal) and the low equilibrium concentrations reported for granular activated carbon (U.S. EPA 1978a; NAS 1980b; Suffet 1980). Toxaphene also has a high Henry's law constant, which may make it amenable to air stripping (Kavanaugh and Trussell 1980).

1.3.2.18 Trihalomethanes

1.3.2.18.1 Existing Drinking Water Guideline

The current Canadian maximum acceptable concentration of 0.35 $mg{\cdot}L^{-1}$ trihalomethanes in drinking water (Health and Welfare Canada 1979a) is based on the conclusion that this concentration would pose a negligible hazard, particularly with respect to the incidence of cancer (Health and Welfare Canada 1980).

Formation of trihalomethanes is related to the water treatment process; thus, the raw water quality in terms of precursor availability and concentration is important. Efforts should be made to minimize the presence of THM precursors in raw water supplies.

1.3.2.18.2 Canadian Exposure

Average daily exposures of Canadians to trihalomethanes are difficult to project because of variabilities in location and drinking water quality. Reported estimates of intake for larger industrialized centres range from 0.1 $mg \cdot d^{-1}$ in winter to 0.25 $mg \cdot d^{-1}$ in summer (Health and Welfare Canada 1980). Drinking water could constitute a large fraction of the intake.

1.3.2.18.3 Water Treatment

As suggested by data from Canadian surveys, raw water sources would be expected to contain little, if any, trihalomethanes (Health and Welfare Canada 1980). If necessary, treatment processes such as intensive air stripping or activated carbon adsorption could be employed for trihalomethane removal (American Water Works Association 1982).

Trihalomethanes (or other halogen-substituted single carbon compounds) are formed by the reaction of a halogen, such as chlorine, with a precursor, such as humic or fulvic acid. There have been considerable study and literature devoted to the surveillance, generation and control of trihalomethanes, and the following discussion only highlights basic treatment considerations. There are three basic control strategies: removal of precursors; removal of produced trihalomethanes; and use of alternative disinfection approaches. Precursor control and disinfection considerations have certain advantages. The former could involve processes such as source treatment and control, activated carbon adsorption, coagulation or precipitation/filtration or oxidation by ozone or potassium permanganate. Chlorine impact modifications include the use of chloramines and alternative application points. In any respect, trihalomethane generation can be controlled, but the trihalomethane formation potential of the raw water substantially dictates the measures required (American Water Works Association 1982).

1.3.3 Physical Parameters

1.3.3.1 Colour

1.3.3.1.1 Existing Drinking Water Guideline

Although the presence of colour may be indirectly linked to health, the primary concern relates to aesthetics (Health and Welfare Canada 1980). The current Canadian maximum acceptable level of 15 true colour units (TCU) is based on detectable colour in a glass of water (Health and Welfare Canada 1979a). Control of colour in drinking water also provides other potential benefits, e.g. removal of potentially toxic chemicals.

1.3.3.1.2 Canadian Exposure

Because colour is measured by a relative, qualitative scale, it cannot be quantified for intake estimation. Reported colour values for Canadian drinking water are not readily available (Health and Welfare Canada 1980).

1.3.3.1.3 Water Treatment

Applicable processes for the removal of colour depend on the nature of the colour-causing agents, such as organic matter or dissolved metals, and other raw water characteristics. Generally, colour in most surface waters originates from humic substances, notably dissolved fulvic acids (American Water Works Association 1971; Health and Welfare Canada 1980). Coagulation and filtration have been the dominant conventional colour removal mechanisms. Alum coagulation/flocculation is effective over rather narrow (pH) treatment conditions, although polyelectrolytes can be of benefit (American Water Works Association 1971; Scheuch and Edzwald 1981; Edwards and Amirtharajah 1985). Other treatment processes employing ozone can also be effective (Constantine 1982). Even with optimum conditions, residual colour remains, and removals in the order of 90% generally reflect careful process selection, control and operation (Scheuch and Edzwald 1981; Krofta and Wang 1982; Edwards and Amirtharajah 1985).

1.3.3.2 Odour

1.3.3.2.1 Existing Drinking Water Guideline

Although odour is considered to be an indicator of potential quality or waterworks problems, a quantitative maximum acceptable limit cannot be established because of the lack of an objective measurement method (Health and Welfare Canada 1980). The current Canadian Drinking Water Quality Guidelines 1978 uses "inoffensive odour" as the guideline (Health and Welfare Canada 1979a).

1.3.3.2.2 Canadian Exposure

No quantitative or qualitative data are available on water-related odour occurrences in Canada. With the diversity of water supplies and treatment, it is suspected that there have been site-specific exposures to a great variety of odours in drinking water (Health and Welfare Canada 1980).

1.3.3.2.3 Water Treatment

Many water treatment processes concomitantly remove odour or odour-causing substances in connection with other treatment goals. These include the basic processes of chemical oxidation, disinfection, coagulation-flocculation and filtration. In addition, specific processes can be applied for odour control, such as aeration or air stripping, chemical oxidation (chlorine, chlorine dioxide, ozone, potassium permanganate) and activated carbon adsorption (American Water Works Association 1971; Baker 1981). It is expected that technology exists to control most odour situations, but economic and operational feasibilities may preclude some applications.

Under certain conditions, odours can be generated during treatment because of incomplete destruction or chemical reactions. For example, chlorination could cause the formation of nitrogen trichloride or chlorophenols (American Water Works Association 1971).

Odour control and prevention are generally site-specific, and the measures used will depend on the nature of the raw water and the available technology appropriate for a particular facility.

1.3.3.3 Turbidity

1.3.3.3.1 Existing Drinking Water Guideline

Turbidity control is considered important for both health and aesthetic reasons. Health-related considerations include disinfection efficiency, biological nutrient availability, trihalomethane formation and concentrations of heavy metals and biocides. The current Canadian maximum acceptable turbidity limit is 5 NTU (nephelometric turbidity unit) (Health and Welfare Canada 1979a).

1.3.3.3.2 Canadian Exposure

Data on turbidity in Canadian drinking water are not readily available (Health and Welfare Canada 1980). It is expected that facilities providing filtration of surface water supplies would produce water containing between less than 1 and 5 NTU, although higher levels may be encountered with temporal or site variations. Turbidity increases within a distribution system may be generated upon resuspension of depositions or may be the result of biological growths.

1.3.3.3.3 Water Treatment

Turbidity can be controlled using a number of approaches and processes, ranging from selective capture and utilization of raw water to complex multistage treatment process trains. Coagulation, followed by filtration through granular media, is the most widely used process to remove the substances producing turbidity in water. Other processes, such as porous media (diatomaceous earth) filtration, can also be used. Treatment technology is generally available to produce drinking waters with turbidities below 1 NTU. Processes used for turbidity removal frequently benefit treated water quality through the reduction or removal of other constituents (American Water Works Association 1971).

1.3.4 Radiological Parameters

1.3.4.1 Radium, Tritium, Strontium, Cesium and Iodine

1.3.4.1.1 Existing Drinking Water Guidelines

The current Canadian maximum acceptable and target concentrations of selected radionuclides are based on 1/100 and 1/1000, respectively, of the International Commission on Radiological Protection recommended dose limits for occupational exposure for a 2 $L \cdot d^{-1}$ intake (Health and Welfare Canada 1979a). The limits are shown in Table 1-4.

Table 1-4. Maximum Acceptable and Target Concentrations of Selected Radionuclides

Radionuclide	Maximum acceptable concentration ($Bq \cdot L^{-1}$)	Target[1] concentration ($Bq \cdot L^{-1}$)
^{226}Ra	1	0.1
^{3}H	40 000	4000
^{90}Sr	10	1
^{137}Cs	50	5
^{131}I	10	1

[1] Also based on health consideration.

Source: Health and Welfare Canada 1979a.

The guidelines also advise that for two or more radionuclides affecting the same organ or tissue, maximum additive conditions should be satisfied (Health and Welfare Canada 1979a). Further, it is recommended that concentrations in water be as low as reasonably achievable considering socioeconomic factors (Health and Welfare Canada 1980).

1.3.4.1.2 Canadian Exposure

Concentrations of ^{226}Ra, ^{3}H, ^{90}Sr, ^{137}Cs and ^{131}I in Canadian drinking water and general intake contributions, as summarized in the Guidelines for Canadian Drinking Water Quality 1978 – Supporting Documentation, are shown in Table 1-5.

Table 1-5. Radionuclide Concentrations in Canadian Drinking Water and Percentage of Total Intake from Water

Radionuclide	Concentrations in drinking water ($Bq \cdot L^{-1}$)	% of total intake from water
^{226}Ra	0.004-0.007	20
^{3}H	ND[1]	<67
^{90}Sr	0.02	20
^{137}Cs	0.004	2
^{131}I	ND	Negligible

[1] ND = not detected.

Source: Health and Welfare Canada 1980.

1.3.4.1.3 Water Treatment

Readily available information on drinking water treatment for removal of radionuclides is limited and primarily confined to ^{226}Ra. Because of the characteristics of the elements, conventional coagulation-flocculation processes are of variable effectiveness for the soluble isotopes (American Water Works Association 1971).

Removal of up to 25% of ^{226}Ra has been suggested, although variability and control difficulties may exist (U.S. EPA 1978a; Sorg and Logsdon 1980). Lower removal rates of less than 15% and less than 1% have been suggested for ^{90}Sr and ^{131}I, respectively (Sorg and Logsdon 1980). Precipitation processes, such as lime-soda ash softening, appear to be effective for the reduction of ^{226}Ra and ^{90}Sr. Removals of 75-96% of ^{226}Ra have been reported for full-scale groundwater supply plants and 84-95% for pilot-scale operations, with a high pH of 10.5-11 required for maximum removal (Brinck *et al.* 1978; Bennett 1978; Edwards and Amirtharajah 1985). Reported strontium removals were in the 67-96% range (U.S. EPA 1978a; Sorg and Logsdon 1980). Conventional iron and manganese removal plants have produced reductions of 11-53%, with radium removal apparently related to manganese reductions (Matheson 1977).

Special treatment using ion exchange or reverse osmosis also has application. Removals of ^{226}Ra of 70-98% through cation-exchange resins have been indicated for full-scale groundwater facilities (Brinck *et al.* 1978; Bennett 1978; Sorg and Logsdon 1980; Myers *et al.* 1985). Removals of up to 95% of ^{90}Sr through similar media have been reported (Sorg and Logsdon 1980). Reverse osmosis, at operating U.S. plants, has provided high removals (87-98%) of ^{226}Ra (Naylor and Dague 1975; Sorg and Logsdon 1980). Removals of more than 95 and 90% of ^{137}Cs and ^{131}I, respectively, through the reverse osmosis process have also been mentioned (U.S. EPA 1978a).

1.3.5 Microbiological Parameters

1.3.5.1 Microorganisms

1.3.5.1.1 Existing Drinking Water Guidelines

The Guidelines for Canadian Drinking Water Quality 1978 (Health and Welfare Canada 1979a) recommend that:

1. no sample should contain more than 10 total coliform organisms per 100 mL;
2. not more than 10% of the samples taken in a 30-d period should show the presence of coliform organisms;
3. not more than two consecutive samples from the same site should show the presence of coliform organisms; and
4. none of the coliform organisms detected should be fecal coliforms.

It must be emphasized that no bacteriological analysis of water can replace a complete knowledge of the conditions at the source of supply and throughout the distribution system. The most that a bacteriological report can do is prove that, at the time of sampling, bacteria indicating fecal pollution did or did not grow under laboratory conditions from a sample of water. Effective treatment including disinfection should yield water free from any coliform organisms, used as indicator bacteria, no matter how polluted the source water may have been. It should not be inferred that the guidelines will guarantee production of drinking water of adequate quality from every raw water source.

1.3.5.1.2 Canadian Exposure

The microbiological quality of water used as a source of drinking water varies widely from sources which need no treatment to those which are heavily contaminated by microorganisms. Adequate treatment of water ensures that consumers are not exposed to contaminated water.

A discussion on the microorganisms of concern to drinking water quality can be found in Chapter 2, except for viruses and *Giardia lamblia*. The latter is becoming more of a concern in drinking water supplies and is discussed in the following paragraph.

Giardia lamblia (Protozoa) is an intestinal parasite which occurs in humans and most warm-blooded animals. No watershed can be effectively quarantined from *Giardia*. Transmission is through contaminated water and can pass from human to human or from animal reservoirs of infection. Infection is usually from cysts present in the water supply, and as few as 10 are known to have caused giardiasis. Symptoms take from 10 to 15 d to appear, and an infected person can exhibit a wide range of symptoms, from very mild diarrhea to severe diarrhea with cramps and anorexia. The latter acute form lasts only a few days; the duration of the disease is generally about 6-7 weeks (Erlandsen and Meyer 1984).

Viruses differ from bacteria in a number of respects. They are obligatory parasites incapable of replication outside their hosts; thus, they cannot multiply in water. They are not part of the human microflora and are shed only by infected individuals. Viruses occur in polluted waters at concentrations many orders of magnitude lower than coliform bacteria and can survive much longer than the bacteria (Health and Welfare Canada 1980).

None of the generally accepted sewage treatment methods yields virus-free effluent and thus most of the viruses, which are much more infective than bacteria, are discharged into surface waters. Disposal of domestic wastewater effluents and solids on land can lead to viral pollution of groundwater (Health and Welfare Canada 1980).

1.3.5.1.3 Water Treatment

The treatment processes required to produce a good quality drinking water will depend on the raw water source. Modern water treatment can produce a potable water from a highly polluted source, but, when possible, water should be obtained from the best quality source available. Every effort should be made to prevent or control pollution. Close monitoring of raw water quality is required so that treatment processes can be adjusted according to any variation detected.

Water treatment processes such as coagulation-flocculation, sedimentation, filtration and disinfection provide multiple barriers for the removal of pathogenic organisms. Disinfection is a key step to the prevention of waterborne disease occurrences. Proper clarification of the water improves the effectiveness of disinfection. The disinfecting agents commonly used are chlorine and its compounds and ozone (Health and Welfare Canada 1980).

Chlorine, besides being an effective germicide, has other benefits which include colour removal, taste and odour control, suppression of algal growths and precipitation of iron and manganese. It is desirable to maintain a chlorine residual in the distribution system so that biocidal action is present throughout the system. Although a trace of residual chlorine will not protect the system from gross contamination, it will prevent growth of organisms from within, and small invasions from without. It also signifies that the water has been exposed to chlorine for a period of time; when no residual is found, none may have existed (Buelow and Walton 1971). The loss of residual chlorine in a localized area can serve as an indicator that foreign material has entered the system or that other problems exist.

Some concerns have been encountered with the use of chlorine, primarily the formation of halogenated organic compounds. These are discussed in the supporting documentation of the drinking water guidelines (Health and Welfare Canada 1980).

Ozone has been used as an alternative to chlorine for many years. It can also be used to eliminate tastes and odours, and aids in the removal of trace metals, including iron and manganese. It is a powerful disinfectant, and inactivates (besides bacteria) viruses, cysts, fungi and spores which are not susceptible to chlorine disinfection. Ozone has a number of disadvantages: it is produced electrically, therefore must be generated on-site; it is difficult to adjust treatment levels to changes in raw water quality, and ozone residuals cannot be maintained for long periods of time, thus water quality will deteriorate during distribution; and ozone is more expensive than chlorine (Health and Welfare Canada 1980). Chlorine can be used following ozone treatment for the maintenance of a chlorine residual in distribution systems.

Chlorine dioxide has been used as a water system disinfectant. It is a powerful germicide, and does not react with ammonia or nitrogenous compounds to form chloramines as does chlorine; residual chlorine dioxide is always available, yet hardly noticeable through taste and odour (White 1972; Dowling 1974). Chlorine dioxide is not known to form halogenated organic compounds (Health and Welfare Canada 1980). Its main drawback is that at equivalent doses it costs more than chlorine. Some concerns have also arisen over chlorite formation.

Other disinfectants include iodine, bromine, potassium permanganate, silver salts and ultraviolet and ionizing radiation. These agents are usually used in specific situations, such as swimming pools and industrial supplies (White 1972).

When water supplies are obtained from polluted sources, effective treatment must be provided to ensure a safe supply of water. It is suggested that raw water coliform measurements be used to assist in determining treatment requirements as follows:

1. If more than 10% of the raw water samples in any 30-d period have a fecal coliform density greater than 100 per 100 mL or a total coliform density greater than 1000 per 100 mL, the water should receive complete treatment consisting of coagulation-flocculation, sedimentation, filtration and disinfection. Where the total coliform index exceeds 5000 per 100 mL in more than 10% of the samples, auxiliary treatment consisting of prechlorination or presedimentation, or their equivalents, and postchlorination should be used. Other advanced forms of treatment approved by the control agency may be considered equivalent to any of the traditional methods named above.
2. If more than 10% of the raw water samples in any 30-d period have a fecal coliform density in the range 10-100 per 100 mL, or a total coliform density between 100 and 1000 per 100 mL, the water should receive a combination of coagulation-flocculation, sedimentation and filtration (partial treatment), or equivalent advanced forms of treatment approved by the control agency, followed by disinfection.
3. If any raw water sample contains fecal coliforms or if more than 5% of the samples in any consecutive 30-d period have a total coliform density greater than 10 per 100 mL, disinfection is required.

All supplies derived from surface water sources should receive disinfection as a minimum treatment. Supplies obtained from shallow groundwater sources should also receive disinfection as required by the control agency (Health and Welfare Canada 1979a).

Giardia lamblia cysts are killed by boiling, but are relatively resistant to chlorine and iodine. Cysts can be removed by coagulation and flocculation followed by complete filtration and disinfection. Slow-rate sand filtration is also effective. Breakdowns in the process train or shortcuts in water treatment at times of high demand will allow *Giardia* cysts to pass into the distribution system (Erlandsen and Meyer 1984; Anonymous 1985).

Well-managed water treatment systems providing effective disinfection and maintaining a free chlorine residual should provide water of an acceptable virological quality. Both chlorine and ozone can, under the proper conditions, be effective virucides. Chlorine must be in the form of undissociated hypochlorous acid. Generally below pH 8.0, turbidity less than 1 NTU and temperature above 4°C, maintenance of a free chlorine residual of 0.5 $mg \cdot L^{-1}$ for 30 minutes should provide virus-free water. Most enteric viruses have not been tested to determine their chlorine resistance. Ozone has virucidal properties, but the resistance of most viruses to ozone is unknown (Health and Welfare Canada 1980).

1.4 REFERENCES

American Water Works Association. 1971. Water Quality and Treatment: A Handbook of Public Water Supplies. 3rd edition. McGraw-Hill, New York. 654 pp.

American Water Works Association. 1982. Treatment Techniques for Controlling Trihalomethanes in Drinking Water. American Water Works Association.

American Water Works Association/American Society of Civil Engineers/ Conference of State Sanitary Engineers. 1971. Water Treatment Plant Design. American Water Works Association, Inc., New York.

Anonymous. 1985. Giardiasis: the new waterborne disease. J. Am. Water Works Assoc. 77(2): 33.

Baker, M.N. 1981. The Quest for Pure Water: The History of Water Purification from the Earliest Records to the Twentieth Century. Vol. II. 2nd edition. American Water Works Association, New York.

Bennett, D.L. 1978. The efficiency of water treatment processes in radium removal. J. Am. Water Works Assoc. 70: 698-701.

Bishop, P.L. and G. Sansoucy. 1978. Fluoride removal from drinking water by fluidized activated alumina adsorption. J. Am. Water Works Assoc. 70: 554-559.

Brinck, W.L., R.J. Schliekelman, D.L. Bennett, C.R. Bell and I.M. Markwood. 1978. Radium-removal efficiencies in water-treatment processes. J. Am. Water Works Assoc. 70: 31-35.

Buelow, R.W. and G. Walton. 1971. Bacteriological quality vs. residual chlorine. J. Am. Water Works Assoc. 63: 28-35. (Cited in Health and Welfare Canada 1980.)

Choi, W.-W. and K.Y. Chen. 1979a. Evaluation of boron removal by adsorption on solids. Environ. Sci. Technol. 13: 189-196.

Choi, W.-W. and K.Y. Chen. 1979b. The removal of fluoride from waters by adsorption. J. Am. Water Works Assoc. 71: 562-570.

Constantine, T.A. 1982. Advanced water treatment for color and organics removal. J. Am. Water Works Assoc. 74: 310-313.

Dart, F.J. 1983. Recent developments in iron and manganese control. *In* Proc. Am. Water Works Assoc. Annu. Conf., June 5-9, Las Vegas, Nevada.

Dobbs, R.A. and J.M. Cohen. 1980. Carbon Adsorption Isotherms for Toxic Organics. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/8-80-023.

Dowling, L.T. 1974. Chlorine dioxide in potable water treatment. Water Treat. Exam. 23: 190-200. (Cited in Health and Welfare Canada 1980.)

Edwards, G.A. and A. Amirtharajah. 1985. Removing color caused by humic acids. J. Am. Water Works Assoc. 77: 50-57.

Edzwald, J.K., J. McIntyre, R.L. Sanks, M.J. Semmens and J.S. Taylor. 1979. Organics removal by coagulation: a review and research needs. J. Am. Water Works Assoc. 71: 588-603.

Erlandsen, S.L. and E.A. Meyer (eds.). 1984. *Giardia* and Giardiasis: Biology, Pathogenesis, and Epidemiology. Plenum Press, New York. 407 pp.

Gomella, C. 1972. Ozone practices in France. J. Am. Water Works Assoc. 64: 39-45.

Guter, G.A. 1982. Project Summary – Removal of Nitrate from Contaminated Water Supplies for Public Use. Final Report. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Guyer, G., P. Adkisson, K. DuBois, C. Menzie and H.P. Nicholson. 1971. Toxaphene Status Report. U.S. Environmental Protection Agency, Washington, D.C. EPA-540/9-71/005.

Hayward, S.B. 1984. Field monitoring of chrysotile asbestos in California waters. J. Am. Water Works Assoc. 76(3): 66-73.

Health and Welfare Canada. 1979a. Guidelines for Canadian Drinking Water Quality 1978. Supply and Services Canada, Hull.

Health and Welfare Canada. 1979b. A National Survey for Asbestos Fibres in Canadian Drinking Water Supplies. Environmental Health Directorate. 79-EHD-34.

Health and Welfare Canada. 1980. Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Hull.

Hess, A.F., J.E. Dyksen and H.J. Dunn. 1983. Control strategy – aeration treatment technique. *In* Occurrence and Removal of Volatile Organic Chemicals from Drinking Water: Cooperative Research Report. American Water Works Association Research Foundation/Keuringsinstituut Voor Waterleidingartikelen, Denver, Colorado/Rijswijk, The Netherlands. 248 pp.

Hickman, R. 1984. Panel: Hazards in drinking water. *In* Critical Issues – Drinking Water. Natl. Conf. on Critical Issues in Drinking Water Quality. Federation of Associations on the Canadian Environment (FACE), February 6-7, Ottawa. pp. 90-98.

Hornung, S.M., J. Yuan and M. Ghosh. 1983. Selenium removal in fixed bed activated alumina adsorbers. *In* Proc. Am. Water Works Assoc. Annu. Conf., June 5-9, Las Vegas, Nevada.

Hrubec, J., M.J. 't Hart, P. Marsman and J.A. Luijten. 1984. Impact of chlorine, chlorine dioxide and ozone on the oxidation of NTA during drinking water treatment. Bull. Environ. Contam. Toxicol. 33: 548-555.

Huang, C.P. and D.W. Blankenship. 1984. The removal of mercury(II) from dilute aqueous solution by activated carbon. Water Res. 18: 37-46.

Karalekas, P.C., Jr., C.R. Ryan and F.B. Taylor. 1983. Control of lead, copper, and iron pipe corrosion in Boston. J. Am. Water Works Assoc. 75: 92-95.

Kavanaugh, M.C. and R.R. Trussell. 1980. Design of aeration towers to strip volatile contaminants from drinking water. J. Am. Water Works Assoc. 72: 684-692.

Krause, T.L. and E.L. Stover. 1982. Evaluating water treatment techniques for barium removal. J. Am. Water Works Assoc. 74: 478-485.

Krofta, M. and L.K. Wang. 1982. Potable water treatment by dissolved air flotation and filtration. J. Am. Water Works Assoc. 74: 305-310.

Leduc, G., R.C. Pierce and I.R. McCracken. 1982. The Effects of Cyanides on Aquatic Organisms with Emphasis Upon Freshwater Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 19246.

Lee, C.F. 1967. Kinetics of reactions between chlorine and phenolic compounds. *In* Principles and Applications of Water Chemistry. Proc. 4th Rudolfs Research Conf. S.D. Faust and J.V. Hunter (eds.). John Wiley & Sons, Inc., New York.

Lee, S.Y. and E.A. Bondietti. 1983. Removing uranium from drinking water by metal hydroxides and anion-exchange resin. J. Am. Water Works Assoc. 75: 536-540.

Logsdon, G.S. and J.M. Symons. 1973. Mercury removal by conventional water-treatment techniques. J. Am. Water Works Assoc. 65: 554-562.

Logsdon, G.S., G.L. Evavold, J.L. Patton and J. Watkins, Jr. 1983. Filter plant design for asbestos fiber removal. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.) 109: 900-914.

Lutwick, G.D. 1980. Arsenic Removal From Well Waters: A Synopsis. Nova Scotia Research Foundation Corporation, Dartmouth, Nova Scotia. 25 pp.

Malaiyandi, M., D.T. Williams and R. O'Grady. 1979. A national survey of nitrilotriacetic acid in Canadian drinking water. Environ. Sci. Technol. 13: 59-62.

Matheson, D.H. 1977. Nitrilotriacetic Acid (NTA) in the Canadian Environment. Water Quality Branch, Inland Waters Directorate, Environment Canada. Sci. Ser. No. 74.

McCreary, J.J. and V.L. Snoeyink. 1977. Granular activated carbon in water treatment. J. Am. Water Works Assoc. 69: 437-444.

McDonald, R.A. 1986. Personal communication. M·R·2 – McDonald & Associates Consulting Engineers, Regina, Saskatchewan.

Méranger, J.C., K.S. Subramanian and C. Chalifoux. 1979. A national survey for cadmium, chromium, copper, lead, zinc, calcium, and magnesium in Canadian drinking water supplies. Environ. Sci. Technol. 13: 707-711.

Myers, A.G., V.L. Snoeyink and D.W. Snyder. 1985. Removing barium and radium through calcium cation exchange. J. Am. Water Works Assoc. 77(5): 60-66.

NAQUADAT. 1980. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

NAS. 1980a. Drinking Water and Health. Vol. 3. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NAS. 1980b. Drinking Water and Health. Vol. 2. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NAS. 1982. Drinking Water and Health. Vol. 4. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Naylor, L.M. and R.R. Dague. 1975. Simulation of lead removal by chemical treatment. J. Am. Water Works Assoc. 67: 560-564.

NRCC. 1982. Effects of Inhaled Particles on Human Health: Influence of Particle Size and Shape. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18564.

Pierce, R.C. 1978. The Aqueous Chlorination of Organic Compounds: Chemical Reactivity and Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16450.

Prakash, A. 1976. NTA (nitrilotriacetic acid) – An Ecological Appraisal. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15023.

Rice, R.G., C.M. Robson, G. Wade Miller and A.G. Hill. 1981. Uses of ozone in drinking water treatment. J. Am. Water Works Assoc. 73: 44-57.

Robeck, G.G., K.A. Dostal, J.M. Cohen and J.F. Kreissl. 1965. Effectiveness of water treatment processes in pesticide removal. J. Am. Water Works Assoc. 57: 181-199.

Rudd, J.W.M. and R.D. Hamilton. 1972. Biodegradation of trisodium nitrilotriacetate in a model aerated sewage lagoon. J. Fish. Res. Board Can. 29: 1203-1208.

Scheuch, L.E. and J.K. Edzwald. 1981. Removing color and chloroform precursors from low turbidity waters by direct filtration. J. Am. Water Works Assoc. 73: 497-503.

Semmens, M.J. and K. Ayers. 1985. Removal by coagulation of trace organics from Mississippi River water. J. Am. Water Works Assoc. 77(5): 79-84.

Shen, Y.S. 1973. Study of arsenic removal from drinking water. J. Am. Water Works Assoc. 65: 543-548.

Sigworth, E.A. 1965. Identification and removal of herbicides and pesticides. J. Am. Water Works Assoc. 57: 1016-1022.

Singleton, H.J. 1986. Water Quality Criteria for Cyanide. Technical Appendix. Water Management Branch, British Columbia Ministry of Environment, Victoria, British Columbia.

Sorg, T.J. 1978. Treatment technology to meet the interim primary drinking water regulations for inorganics. J. Am. Water Works Assoc. 70: 105-112.

Sorg, T.J. 1979. Treatment technology to meet the interim primary drinking water regulations for organics: Part 4. J. Am. Water Works Assoc. 71: 454-466.

Sorg, T.J. and G.S. Logsdon. 1978. Treatment technology to meet the interim primary drinking water regulations for inorganics: Part 2. J. Am. Water Works Assoc. 70: 379-393.

Sorg, T.J. and G.S. Logsdon. 1980. Treatment technology to meet the interim primary drinking water regulations for inorganics: Part 5. J. Am. Water Works Assoc. 72: 411-422.

Sorg, T.J., M. Csanady and G.S. Logsdon. 1978. Treatment technology to meet the interim primary drinking water regulations for inorganics: Part 3. J. Am. Water Works Assoc. 70: 680-691.

Steiner, J., IV and J.E. Singley. 1979. Methoxychlor removal from potable water. J. Am. Water Works Assoc. 71: 284-286.

Suffet, I.H. 1980. An evaluation of activated carbon for drinking water treatment: A National Academy of Science report. J. Am. Water Works Assoc. 72: 41-50.

Toft, P., D. Wigle, J.C. Méranger and Y. Mao. 1981. Asbestos and drinking water in Canada. Sci. Total Environ. 18: 77-89.

U.S. EPA. 1978a. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/8-77-005.

U.S. EPA. 1978b. Interim Treatment Guide for Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon. Supporting Documentation for U.S. Environmental Protection Agency Interim Primary Drinking Water Regulations, "Control of Organic Chemical Contaminants in Drinking Water". J.M. Symons (ed.). Water Supply Research Division, Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

U.S. EPA. 1979. Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a.

U.S. EPA. 1980. Ambient Water Quality Criteria for Antimony. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-020.

van Lier, W.C., E. Schultinkvj van Soest, B. van der Ver, J. Roelands and B. Visser. 1983. Experience with granular activated carbon filters on pilot plant scale. *In* Activated Carbon in Drinking Water Technology. Keuringsinstituut Voor Waterleidingartikelen, American Water Works Association Research Foundation.

Watkins, J., Jr., R.A. Ryder and W.A. Persich. 1978. Investigation of turbidity, asbestos fibers, and particle counting techniques as indices of water treatability of a Cascade mountain water source. *In* Proc. Am. Water Works Assoc. Annu. Conf., June 25-30, Atlantic City, New Jersey.

White, G.C. 1972. Handbook of Chlorination: for Potable Water, Wastewater, Cooling Water, Industrial Processes, and Swimming Pools. Van Nostrand Reinhold Co., Cincinnati, Ohio. 744 pp. (Cited in Health and Welfare Canada 1980.)

White, S.K. and E.A. Bondietti. 1983. Removing uranium by current municipal water treatment processes. J. Am. Water Works Assoc. 75: 374-380.

Wiley, J.O. and P.O. Nelson. 1984. Cadmium adsorption by aerobic lake sediments. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.) 110: 226-243.

Wood, P.R. and J. DeMarco. 1979. Treatment of groundwater with granular activated carbon. J. Am. Water Works Assoc. 71: 674-682.

2.0 RECREATIONAL WATER QUALITY AND AESTHETICS

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2.0 RECREATIONAL WATER QUALITY AND AESTHETICS

2.1 INTRODUCTION

Recreational water refers to surface waters that are used primarily for sports in which the user comes into frequent direct contact with the water, either as part of the activity or incidental to the activity, e.g. swimming and board-sailing. Other recreational uses include boating, canoeing and fishing which generally have less frequent body contact with water.

The guidelines contained in this chapter deal mainly with potential health hazards related to recreational water use, but also relate to aesthetics and nuisance conditions. Health hazards associated with direct recreational contact with water include infections transmitted by pathogenic microorganisms and injuries resulting from impaired visibility in turbid waters.

The water quality characteristics of importance to the recreational use of water are given in Table 2-1. The guidelines recommended in the Guidelines for Canadian Recreational Water Quality prepared for the Federal-Provincial Advisory Committee on Environmental and Occupational Health (Health and Welfare Canada 1983) are summarized in Table 2-2.

A discussion of sampling and enumeration of microbiological indicators of recreational water quality can be found in the Guidelines for Canadian Recreational Water Quality (Health and Welfare Canada 1983).

Table 2-1. Water Quality Characteristics of Importance to Recreational Water Use

Characteristic	Swimming[1]	Nonswimming
Microbiological		
Indicator organisms		
Fecal coliforms	x	
Total coliforms	x	
Fecal streptococci	x	
Enterococci	x	
Escherichia coli	x	
Coliphages	x	
Pathogens	x	
Pseudomonas aeruginosa	x	
Giardia lamblia	x	
Nuisance		
Vector and nuisance organisms	x	x
Aquatic vascular plants	x	x
Phytoplankton	x	x
Physical and chemical		
pH	x	
Temperature	x	
Aesthetics	x	x
Oil, debris	x	x
Clarity	x	
Turbidity	x	
Colour	x	

[1] Swimming also includes sail boarding, water skiing, white water sports, scuba diving and dinghy sailing.

2.2 GENERAL REQUIREMENTS

2.2.1 Health and Safety Related

Water used for recreational purposes should be sufficiently free from fecal contamination, pathogenic organisms and other hazards, e.g. poor visibility, to protect the health and safety of the user (Health and Welfare Canada 1983).

The determination of the risk of infection is based on a number of factors, including (1) results of a sanitary survey; (2) results of epidemiological studies; (3) fecal coliform counts; and (4) the presence of pathogens (Health and Welfare Canada 1983).

The National Academy of Sciences (NAS 1977) has listed the ideal characteristics for organisms that are indicators of fecal contamination. They are as follows:

1. suitable for use in all types of water;
2. present in sewage and polluted waters when pathogens are present;
3. present in numbers which are correlated to the degree of pollution;
4. present in greater numbers than pathogens;
5. do not proliferate in the aquatic environment;
6. survive for longer periods in the environment than do pathogens;
7. absent from unpolluted waters;
8. readily detected by simple and accurate laboratory methods; and
9. harmless to humans and animals.

2.2.2 Visual, Aesthetics

The local setting of recreational water bodies is of prime importance, as the surrounding countryside has a strong visual effect on the enjoyment of lakes and rivers, whether the activity is physically active or passive, such as gazing on the scenery.

In northern waters, swimming is not a major recreational activity, and factors other than microbiological are major components when determining the suitability of lakes and rivers and their environs as recreational areas. Visual impact of the whole area is as important as the quality of the water.

Impacts on a water source come from many activities. These include logging, mining, drainage of wetlands, dredging, dam construction, agricultural runoff, industrial and municipal wastes, land erosion, road construction and land development. These factors all have to be considered in areas of natural beauty which are used for the many recreational activities engaged in by Canadians and visitors to Canada.

2.3 MICROBIOLOGICAL CHARACTERISTICS

2.3.1 Indicator Organisms of Health Risk for Swimming Areas

A number of organisms have been considered as indicators of health risk for swimming areas. These include the fecal coliform and enterococci bacteria. Fecal coliforms have been

Table 2-2. Summary – Guidelines for Recreational Water Quality

Parameter	Guideline	Parameter	Guideline
Bacteriological Fecal coliforms	The geometric mean of not less than 5 samples taken over a 30-d period should be less than 200 fecal coliforms per 100 mL. Resampling should be performed when any sample exceeds 400 fecal coliforms per 100 mL.	Aesthetics	All water should be free from: – materials that will settle to form objectionable deposits; – floating debris, oil, scum and other matter; – substances producing objectionable colour, odour, taste or turbidity; and – substances and conditions or combinations thereof in concentrations which produce undesirable aquatic life.
Pathogens Coliphages Enterococci *E. coli* *P. aeruginosa* *G. lamblia*	))) see text)))		
Clarity	The water should be sufficiently clear that a Secchi disc is visible at a minimum of 1.2 m.	Oil and grease	Oil or petrochemicals should not be present in concentrations that: – can be detected as a visible film, sheen or discolouration on the surface; – can be detected by odour; or – can form deposits on shorelines and bottom deposits that are detectable by sight and odour.
pH	5.0-9.0, provided that when the pH is near the extremes of this range, the buffering capacity of the water is very low.		
Turbidity[1]	The turbidity of water should not be increased more than 5.0 NTU over natural turbidity when this is low. (<50 NTU)	Aquatic plants	Rooted or floating plants which could entangle bathers should be absent; very dense growths could affect other activities such as boating and fishing.

[1] Singleton 1986.

Source: Health and Welfare Canada 1983.

used as a fecal pollution indicator for many years because of ease of measurement, but counts do not correlate well with the incidence of gastrointestinal (GI) illness and use of this group is being phased out. Recent improvements in detection and measurement techniques enable the use of organisms which give a more reliable indication of health risk. These organisms include enterococci, the fecal coliform *Escherichia coli* and the pathogen *Pseudomonas aeruginosa*, which causes ear infections (otitis externa). *Pseudomonas aeruginosa*, as an opportunistic pathogen, strictly should not be classified as an indicator organism; however, it is utilized in this manner.

Some Canadian provinces, the International Joint Commission, the U.S. Environmental Protection Agency and some U.S. states have recommended or are in the process of recommending the use of one or more of the following microorganisms – *E. coli*, enterococci and *P. aeruginosa* – as indicator organisms for health risk assessment at swimming beaches. Recent studies using these organisms allow a more accurate assessment to be made of the risk of becoming ill from exposure to pathogens at bathing beaches. Dufour (1984) showed that there was a direct linear relationship between the rate of swimming-associated gastrointestinal illness and the densities of both *E. coli* and enterococci. Either organism could be used as a reliable indicator of fecal contamination. The current Guidelines for Canadian Recreational Water Quality (Health and Welfare Canada 1983) have the flexibility to take these developments into account and the phasing in of measurements of these organisms will be considered when their assessment as indicators is completed.

The following text discusses the guidelines for microbiological characteristics of bathing beaches, found in the Guidelines for Canadian Recreational Water Quality (Health and Welfare Canada 1983). These recognize that some provinces have more restrictive requirements which relate directly to local conditions. Brief discussions on the more recent guidelines from other agencies can also be found below.

A number of procedures for use in assessing recreational water quality have been reviewed by a committee responsible for watershed management in the Toronto area: (1) development of a methodology to evaluate the effect of wet-weather bacterial densities in interpreting water quality objectives; (2) selection of sampling stations by considering the water source and water-use locations and factors affecting bacterial transport in streams and rivers; (3) sediment phase monitoring to permit detailed mass balance computations; (4) estimation of bacterial growth and die-off rates; and (5) bacterial inputs from other sources such as waterfowl, mammals, etc. (Toronto Area Watershed Management Strategy Steering Committee 1985).

2.3.1.1 Fecal Coliforms

2.3.1.1.1 Guideline

Until the Federal-Provincial Advisory Committee on Environmental and Occupational Health revises the guideline, the following recommendation is made.

The geometric mean of not less than five samples taken over a 30-d period should be less than 200 fecal coliforms per

100 mL. Resampling should be performed when any sample exceeds 400 fecal coliforms per 100 mL (Health and Welfare Canada 1983).

The exact risk associated with bathing in waters of this quality cannot be established, but it is probably quite low, corresponding to about a 0.12-1.5% chance of contracting gastrointestinal illness, on the basis of epidemiological data. It does not give any estimate of the risk associated with pathogens from nonfecal sources or very long-lived organisms (Health and Welfare Canada 1983). The presence of 200 fecal coliforms per 100 mL has been reported to allow a 0.6% gastrointestinal illness rate (McGovern 1983).

2.3.1.1.2 Rationale

Most Canadian recreational waters are of high microbiological quality, but certain waters are contaminated throughout all, or part, of the bathing season. Fecal coliforms range in concentration from essentially undetectable in many recreational waters to tens of thousands per litre in areas directly affected by sewage discharges.

The definitive fecal coliform is considered to be *Escherichia coli* (see Section 2.3.1.5). It comprises about 97% of the coliform organisms in human feces, with *Klebsiella* comprising 1.5% and *Enterobacter* and *Citrobacter* together another 1.7% (Dufour 1977). *Escherichia coli* is also found in feces from birds and mammals. Fecal coliforms are useful indicators of feces-contaminated water because they are present in virtually all warm-blooded animals in numbers far exceeding such pathogens as *Pseudomonas aeruginosa*, *Salmonella*, *Shigella*, *Vibrio* and *Clostridium*; however, the relationships are variable and illness is not always associated with elevated densities of indicator organisms. It has been shown that the concentration of viruses does not correlate well with the concentration of fecal coliforms (Berg and Metcalf 1978).

Analyses of fecal coliforms in Canadian fresh waters have revealed that, although the numbers of *E. coli* vary quite widely, they usually comprise a high percentage of the fecal coliform counts (Vlassoff 1981).

The following gives some historical background on the use of fecal coliforms as indicators of risk for swimming-associated gastroenteritis occurrence. Studies conducted by the U.S. Public Health Service during the early 1950's on the Ohio River showed that a count of 2300-2700 total coliforms per 100 mL was the threshold for finding significant illness effects from water pollution. A study at the same location in the 1960's showed that a fecal coliform count of 400 per 100 mL of river water was approximately equivalent to the earlier total coliform counts (Geldreich 1966). After application of a safety factor, 200 fecal coliforms per 100 mL was recommended as the limit (Federal Water Pollution Control Administration 1968).

A major consideration against using the fecal coliform count to estimate the risk of becoming ill after swimming at bathing beaches is the input of fecal coliforms from sources other than feces. The ratio of fecal coliform to *Escherichia coli* (see Section 2.3.1.5) can change greatly in waters that receive industrial effluents. This is probably because of the large numbers of *Klebsiella* sp. which show up in the counts as fecal coliforms, but are not of fecal origin. The types of industries identified to date are food, dairy and pulp and paper industries (Leggatt 1986). *Escherichia coli* has recently been considered to be a more accurate indicator.

2.3.1.2 Total Coliforms

No maximum acceptable limit for total coliform organisms has been set (Health and Welfare Canada 1983).

2.3.1.3 Fecal Streptococci

No limit for fecal streptococci has been proposed. It is recommended that fecal streptococci data be used to support information in water quality surveys and assist in determining the nature and extent of pollution in surface waters (Health and Welfare Canada 1983).

2.3.1.4 Enterococci

Recent studies have shown significant relationships between the density of enterococci and gastrointestinal disease caused by swimming in fresh water (Dufour 1984); however, until standard laboratory protocols have been accepted and are familiar to all provinces, no guideline will be recommended in this publication. Future editions should be able to take this indicator into account, keeping in mind that when using enterococcus as an indicator, the media, the membrane brand and the technique used must be standardized if the indicator is to be of value.

The recommendation on microbiological indicators for the Great Lakes, presented to the International Joint Commission in 1983 (IJC 1983), stated that the geometric mean level of enterococci, using the mE medium (U.S. EPA 1985), should not exceed 11 per 100 mL. Mean levels should be monitored by analyzing a minimum of five samples from one location over a 4-week period. This is the lowest statistically significant detectable indicator level associated with the onset of gastrointestinal swimming-associated illness. "No-effect" levels cannot be measured (IJC 1983).

The Aquatic Ecosystem Objectives Committee (IJC Great Lakes Science Advisory Board) recommends the use of the following regression equation to base local guidelines on the incidence of GI illness rates per 100 000 persons. This is also illustrated in Figure 2-1 (Dufour 1982). The graph showing the relationship of GI illness rates to enterococci densities was developed from a number of data points, but the lowest highly statistically significant effect level for enterococci was observed at a density of 11 per 100 mL.

$$y = -213.2 + 613.8 \log x_1$$

where y = illness rate per 100 000 persons

x_1 = number of enterococci per 100 mL.

The U.S. EPA asked for comments on their proposed criterion of 20 enterococci per 100 mL. This is equated with a risk of 0.6% GI illness rate (Anonymous 1984). This recommendation was amended to "not to exceed 33 enterococci per 100 mL" after receipt of comments (Anonymous 1986; U.S. EPA 1986) (see Section 2.3.1.5).

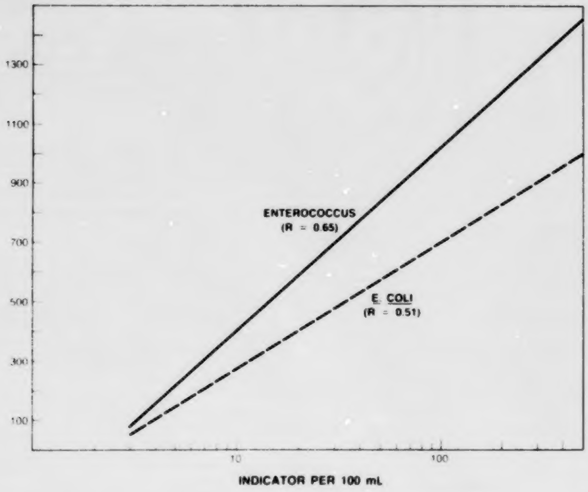

Figure 2-1. **Swimming-associated rate for highly credible GI symptoms per 100 000 persons.**

2.3.1.5 *Escherichia coli*

The use of *E. coli* instead of the fecal coliform group has been recommended by the IJC, some Canadian provinces and the U.S. EPA. *Escherichia coli* inhabits the gastrointestinal tract of humans (comprising about 97% of the coliforms found in human feces) and other warm-blooded animals, and therefore can be used as specific indicators of fecal pollution since it is rarely found growing in natural habitats.

The levels of *E. coli* in aquatic habitats range from less than 10 L^{-1} in some recreational lakes to thousands per litre in surface water contaminated with sewage or stormwater. Recent epidemiological studies have found a strong relationship between levels of *E. coli* in recreational water and the incidence of swimming-associated gastrointestinal symptoms (Dufour 1984). This organism can be related only to the incidence of gastrointestinal upsets and not to other swimming-associated ailments.

The IJC recommends that the seasonal geometric mean level of *E. coli* (enumerated by the mTEC procedure) in the Great Lakes should not exceed 23 per 100 mL. Mean levels should be monitored and used to apply this limit by analyzing a minimum of five samples from one location collected over a 4-week period. The mTEC procedure refers to the method and media used by Dufour (1982). This is a membrane filter test which produces counts of only the *E. coli* (mTEC), and is the method recommended by the IJC (1983). The values specified are the lowest statistically significant detectable indicator levels associated with the onset of GI swimming-associated illness. "No-effect" levels cannot be measured. The following regression equation allows the assessment of GI illness rates per 100 000 persons (Figure 2-1) (Dufour 1982).

$$y = -150.5 + 423.5 \log x_2$$

where y = illness rate per 100 000 persons
x_2 = number of *E. coli* per 100 mL.

An Ontario Ministry of the Environment/Ministry of Health Expert Committee reviewed the current Ontario Recreational Use Guidelines and recommended adoption of a new guideline based on *E. coli* to provide a measure of protection against the risk of gastrointestinal illness for bathers, and on *Pseudomonas aeruginosa* to provide a measure of protection for swimmers from otitis externa (swimmer's ear). This Expert Committee's recommendations will be considered by another External Committee which will include input from the public (Leggatt 1986).

The U.S. EPA asked for comments on their proposed criterion for *E. coli* of 77 per 100 mL, allowing a 0.6% GI illness rate (Anonymous 1984). This was amended, after comments, to "not to exceed 126/100 mL" (Anonymous 1986). This is calculated as the seasonal geometric mean of a statistically significant number of samples, generally not less than five samples equally spaced over a 30-d period. Different confidence levels are recommended for four levels of swimming use: no sample should exceed a one-sided confidence limit (C.L.) calculated using the following as guidance:

designated bathing beach	75% C.L.
moderate use for bathing	82% C.L.
light use for bathing	90% C.L.
infrequent use for bathing	95% C.L.

based on a site-specific log standard deviation, or if site data are insufficient to establish a log standard deviation, then using 0.4 as the log standard deviation for both indicators (U.S. EPA 1986). The U.S. EPA expects a gradual transition from the use of fecal coliforms to the use of *E. coli* or enterococci (Anonymous 1986).

2.3.1.6 Coliphages

Coliphages have been suggested as indicators of the presence of enteric pathogens, especially when it takes longer than 24 h for water samples to reach the laboratory. Studies have indicated that 3-9 fecal coliforms = 1 coliphage, and it has been suggested that 200 coliphages per litre is an indication of degraded water (Dutka 1986); however, some authors state that further research is needed to ensure that coliphages are a reliable indicator (McNeill 1985). The method for coliphage detection (tentative) and formulae for estimating the number of fecal coliforms from coliphage counts are given in the American Public Health Association's Standard Methods (Greenberg *et al.* 1985).

Coliphage is the term given to bacterial viruses which infect and replicate in fecal coliforms, coliforms and *E. coli*. Because coliphages replicate only in these organisms, the presence of coliphage also indicates the probable presence of these indicators.

Coliphages are shed at high levels by humans and other warm-blooded animals, and indicate that fecal material, possibly containing surviving pathogenic enteroviruses, is present. Some coliphages are more resistant to environmental conditions and chlorination than are most enteroviruses, so that the elimination of the latter can be assumed to have occurred if these coliphages cannot be found. However, there are circumstances under which coliphage detection may not accurately indicate the presence of enteroviruses (U.S. EPA 1984).

Detection of waterborne coliphages is easier than detection of enteroviruses because:

1. they are present in greater numbers than enteroviruses in fecal material and therefore in fecal-contaminated water; and
2. they can be isolated and counted by relatively simple means, and in less time than is required for enteroviruses (coliphage enumerations can often be accomplished within 4-6 h, whereas 7-8 d are required for enterovirus enumerations [Kott *et al.* 1978]).

If coliphages are to be used as an indicator, it is essential that the method used for detection is the same each time, using one medium and one membrane type, as deviations from these will affect the counts. The technique used must be an approved one.

2.3.2 Pathogens

No maximum limits were proposed in the Guidelines for Canadian Recreational Water Quality 1983 (Health and Welfare Canada 1983) for the following microbiological organisms: *Candida albicans*; *Pseudomonas aeruginosa*; *Salmonella*; *Shigella*; *Staphylococcus aureus*; and viruses. Monitoring for some or all of these organisms should be undertaken when it is deemed necessary to obtain a more complete assessment of the quality of specific water-contact recreational areas (Health and Welfare Canada 1983).

2.3.2.1 *Pseudomonas aeruginosa*

Pseudomonas aeruginosa is a potential pathogen and the main etiological agent for ear infections (otitis externa) in swimmers. A relationship has been shown between the numbers of *P. aeruginosa* in the water and the incidence of ear infections (McNeill 1985).

Pseudomonas aeruginosa incidence in human feces is low for healthy individuals (Hoadley 1977), and the organism is rarely isolated from the feces of lower animals (Wheater *et al.* 1979). It is also present on plants and soil, and could be present in surface runoff (McNeill 1985).

The levels of *P. aeruginosa* at bathing beaches will depend on bather density. If the bacterium is present in water, immersing the ear will allow either colonization or infection of the ear canal, although the exact process of infection is not known (Seyfried and Cook 1984).

The IJC (1983) recommended that for the protection of recreational users of nearshore waters from ear infections, no more than 25% of analyses should have levels of *P. aeruginosa* (enumerated by the mPA method) greater than 10 per 100 mL. Under these conditions, the mean or median level of *P. aeruginosa* will usually be less than 1 per 100 mL.

The use of *P. aeruginosa* is currently being evaluated by other agencies; once the assessment is complete, this bacterium could become more widely used as a reliable indicator for estimating the risk of contracting ear infection. It is a necessary component of any in-depth study of bathing beaches (Tobin 1986).

2.3.2.2 *Giardia lamblia*

Authorities in recreational areas are becoming more aware of the risk of *Giardia lamblia* (Protozoa) infection. As few as 10 cysts of the parasite are known to have caused giardiasis. Symptoms take from 10 to 15 d to appear and can range from very mild to severe diarrhea with cramps and anorexia. The acute form lasts a few days but the duration of the disease can be up to 7 weeks. The beaver is one of the more common of the animal reservoirs of the parasite. Infective cysts can be killed by boiling water which is used by campers and cottagers (Laird *et al.* 1980; Erlandsen and Meyer 1984).

2.4 NUISANCE ORGANISMS

2.4.1 Guideline

Some biota which could be a nuisance to bathers if present in large numbers, such as large amounts of rooted or floating macrophytes, phytoplankton scums, filamentous algal mats, sewage fungus, leeches, etc., should be absent from areas intended for development as bathing beaches. The presence of large numbers of midges and aquatic worms, which can tolerate organic pollution, would indicate that the water was not suitable for recreational use.

2.4.2 Rationale

Two principal types of biological factors influence the recreational value of surface waters: (1) those that endanger the health or physical comfort of people and animals and (2) those that render water aesthetically objectionable or unusable as a result of the presence of excessive nutrients or the presence of unsightly substances. The former include vector and nuisance organisms, and the latter, aquatic growth of microscopic and macroscopic plants, and such substances as oil and garbage.

2.4.2.1 Vector and Nuisance Organisms

Massive emergences of nonbiting midges, phantom midges, mayflies, etc., cause serious nuisances in shoreline communities and impede recreational pursuits. In addition to the physical annoyance of their presence, biting insects such as mosquitoes and blackflies can inflict irritation from their biting attacks.

Schistosome dermatitis, or swimmers' itch, is one of the more obvious problems of concern in water-contact sports in Canada. A number of schistosome cercariae, nonspecific for humans, are able to enter the outer layers of human skin. The reaction, or cutaneous inflammatory response, causes itching, and the severity is related to the person's sensitivity and prior exposure history. The most important of the dermatitis-producing cercariae are parasites of waterfowl (Health and Welfare Canada 1983).

Prevention of swimmers' itch can be assured only by complete avoidance of aquatic sports in areas where the disease has been a problem. An acceptable alternative might be the elimination of the molluscan hosts; however, the toxic effects of molluscicides on other aquatic life should be carefully considered. The least expensive molluscicide is copper sulphate, but, when applied as recommended to control "swimmers' itch", it has adverse effects on aquatic life. An alternative to the use of molluscicides, which is less hazardous to water quality, is the removal of pond vegetation. This deprives the snails of a major source of shelter and nourishment. A disadvantage is that other aquatic life is also affected (Health and Welfare Canada 1983).

2.4.2.2 Aquatic Vascular Plants

Aquatic vascular plants (macrophytes), both rooted and nonrooted, can interfere with recreational uses of water. Macrophytes obstruct the view of swimmers and obscure underwater hazards. They can also entangle swimmers and may induce panic, especially if encountered unexpectedly. Boating and fishing may be restricted if the growths are very dense.

Rafts of free-floating plants and attached plants that have been dislodged from the substrate could drift onto beaches and swimming areas. Drying and decaying aquatic plants are unsightly, cause objectionable odours and provide breeding areas for a variety of invertebrates, bacteria and fungal growths.

Increased plant growth can be caused by the introduction of exotic species and by the presence of excess nutrients; for example, various agricultural practices and wastewater inputs may increase the amount of phosphorus and nitrogen. This increase in nutrient loading causes cultural eutrophication. The natural eutrophication of bodies of water occurs much more slowly, and does not change on a time scale to be of significant interest for recreational water quality guidelines. Increased silt loads, changes in shorelines and land use all contribute to alterations in aquatic habitats (Health and Welfare Canada 1983) and these factors are probably more important than nutrients in causing increased growth of some species of nuisance aquatic plants.

2.4.2.3 Phytoplankton

Phytoplankton are free floating microscopic plants which can become a nuisance by rapid increases in numbers. This sometimes creates a situation where the water resembles a "pea soup" or "bloom" condition. This can be a natural phenomenon, but it is often due to accelerated eutrophication caused by human activities.

Attached algae are usually filamentous or colonial forms which adhere to some form of substrate (i.e. rocky bottom, piers, other aquatic vegetation) and may become so abundant as to obscure the true nature of the substrate. These forms may break away from the substrate and create massive shoreline accumulations with similar conditions as cited above for rooted aquatic vegetation.

Toxic algae are found in all aquatic environments, and have been responsible for illness in humans. The most important phyla are Pyrrhophyta (dinoflagellates), Chrysophyta and Cyanophyta (blue-green algae). Algae of concern in lakes and ponds are usually the blue-greens *Anabaena flos-aquae*, *Microcystis aeruginosa* and *Aphanizomenon flos-aquae* (McLeod and Bondar 1952; Senior 1960; Aziz 1974; Moore 1977; Carmichael 1986), though toxic strains of the latter have not been documented in Canada (Brownlee 1986) (see Section 6.6.1).

Fish kills and the death of invertebrates because of blue-green algae have been reported by a number of authors. Massive blooms of freshwater algae often cause die-off of fish and other organisms when the algal populations suddenly collapse. The death and rapid decomposition of the algae quickly lead to anoxia and asphyxiation of fish and other aquatic animals (Prescott 1948; Barica 1975; Nicholls, Kennedy and Hammett 1980).

Some odours from lake water originate from the decomposition of algae and other aquatic plant materials. Several species of algae produce offensive odours while in the active growing state (Palmer 1962; Taft 1965; Neil 1975; Nicholls, Beaver and Estabrook 1980).

Odours from lake water can be measured by the Threshold Odour Test (TON) (Rand *et al.* 1975). The TON is the ratio by which the sample must be diluted with odour-free water so that the odour is just detectable by a test panel. Many natural surface waters not influenced by odour-producing algae have a TON of 5, whereas others with excessive algal growth may have a TON value exceeding 200.

2.5 PHYSICAL AND CHEMICAL CHARACTERISTICS

The following sections discuss some of the physical and chemical characteristics of water that should be considered when areas are being used or proposed for bathing.

2.5.1 pH

2.5.1.1 Guideline

Until more studies have been completed, and the tolerance limits of eyes have been determined, it should be considered acceptable to swim in water with a pH between 5.0 and 9.0, provided that, when the pH is at or near the extremes of this range, the buffering capacity is very low (Health and Welfare Canada 1983). Some provinces may have a more stringent objective than this which relates more directly to their water type.

2.5.1.2 Rationale

To understand the resistance of fresh water to acidification and to translate potential changes in pH into guidelines for body contact, it is important to understand several terms that are related to the acidity of aqueous solutions. A detailed discussion on pH and buffering capacity can be found in Chapter 6 (see Section 6.2.1).

Studies using rabbits and human volunteers showed no harmful effects to external ocular tissues when eyes were exposed to lake water having a pH as low as 4.5 (Basu *et al.* 1984). More studies have been recommended using water with a low pH but greater buffering capacity.

2.5.2 Temperature

There is considerable variation from one individual to another in the rate of body cooling and the incidence of survival in cold water. The variability is a function of body size, fat content, prior acclimatization and overall physical fitness. The ratio of body mass to surface area is greater in large, heavy individuals, and their temperatures change more slowly than that of a small child (Kreider 1964).

The thermal characteristics of water used for bathing and swimming should not cause an appreciable increase or decrease in the deep body temperature of bathers and swimmers. In cold water, heat is lost primarily by conduction from the inner organs through the trunk. Exercise in water increases the loss of body heat and correspondingly decreases survival time. Extended periods of continuous immersion in water colder than 15°C may cause the death of some swimmers, and will be extremely stressful to all swimmers who are not wearing underwater protective clothing.

The upper safe limit of water temperature for recreational immersion varies from individual to individual, and seems to depend on psychological rather than physiological considerations. Unlike that in cold water, the mass surface area ratio in warm water favours the child. Thermal stress would not be experienced under moderate metabolic heat production as long as the water temperature was lower than the normal skin temperature of 33°C. The survival of an individual submerged in water above 34-35°C depends on tolerance to an elevated internal body temperature, and there is a risk of injury with prolonged exposure (Health and Welfare Canada 1983).

2.5.3 Salinity

For water-contact recreation, salinity *per se* does not appear to be a limiting factor, in terms of either concentrations or constituent ions, given that other factors, such as pH and temperature, fall within acceptable ranges. Some ions (magnesium sulphate, sodium sulphate) may have a mildly laxative effect if the water is accidentally swallowed.

In Saskatchewan, recreation facilities are developed and enjoyed on lakes up to 81.4‰ salinity, including all common saline-lake ion constituents (sodium sulphate, magnesium sulphate, sodium carbonate and combinations thereof) (Appleby 1986).

2.5.4 Aesthetics

2.5.4.1 Guideline

All waters should be free from substances attributable to wastewater or other discharges in amounts that would interfere with the existence of life forms of aesthetic value. These include:

1. materials that will settle to form objectionable deposits;
2. floating debris, oil, scum and other matter;
3. substances producing objectionable colour, odour, taste or turbidity; and
4. substances and conditions or combinations thereof in concentrations which produce undesirable aquatic life (Health and Welfare Canada 1983).

2.5.5 Clarity – Light Penetration

2.5.5.1 Guideline

Water should be sufficiently clear that a Secchi disc is visible at a minimum depth of 1.2 m (Health and Welfare Canada 1983).

2.5.5.2 Rationale

The clarity of water is measured by the Secchi disc. It is important that swimming areas are clear enough for users to estimate depth and to see subsurface hazards easily. In "learn to swim" areas, the clarity should be such that a Secchi disc on the bottom is visible.

2.5.6 Turbidity

2.5.6.1 Guideline

The turbidity of water should not be increased more than 5.0 NTU (nephelometric turbidity units) over natural when turbidity is low (<50 NTU) (Singleton 1986). When assessing visibility and safety of swimmers, both turbidity and clarity determinations should be considered.

2.5.6.2 Rationale

Lifeguards and other persons should be able to see and distinguish people in distress at areas used for swimming. In addition, swimmers should be able to see while swimming under water.

2.5.7 Colour

There are two measures of colour – true and apparent. The true colour of natural water is the colour of water from which turbidity has been removed (i.e. filtered water) (Rand *et al.* 1975).

Natural minerals give true colour to water; for example, calcium carbonate in limestone regions gives a greenish colour, ferric hydroxide, red. Organic substances, such as tannin, lignin and humic acids from decaying vegetation, also give true brown colour to water (Reid and Wood 1976).

Apparent colour is usually the result of the presence of coloured particulate matter, the interplay of light on suspended particles and such factors as bottom or sky reflection. An abundance of algae whether it be free floating or attached to the substrate may influence the apparent colour of the water providing a broad spectrum of colours that are dependent on the dominating taxa.

To measure true colour, the water has to be filtered to remove apparent colour. True colour is measured on the platinum-cobalt scale (Pt-Co units), and ranges from very low numbers in clear lakes to over 300 units in the very dark waters of peat bogs (Reid and Wood 1976). Apparent colour is an aesthetic quality and cannot be quantified.

A guideline for the colour of recreational water largely depends on the preference of users, and it is impossible to put an absolute value on it. Colour should not be so intense as to impede visibility in areas used for swimming. A maximum limit of 100 Pt-Co units was proposed by Environment Canada (Environment Canada 1972), but no rationale was given. (A maximum acceptable level of 15 Pt-Co units is proposed by Health and Welfare [Health and Welfare Canada 1979] for drinking water for aesthetic reasons.)

2.5.8 Oil and Grease

2.5.8.1 Guideline

Oil or petrochemicals should not be present in concentrations that:

1. can be detected as a visible film, sheen or discolouration on the surface;
2. can be detected by odour; or
3. can form deposits on shorelines and bottom sediments that are detectable by sight and odour (IJC 1977).

2.5.8.2 Rationale

The presence of oily substances makes water aesthetically unattractive. It is very difficult to establish guidelines for oil and grease, as the mixtures falling under this category are very complex. Contamination of recreational waters with oily substances may occur as a result of natural or man-made causes. Decaying vegetation (terrestrial or aquatic) will, in the advanced state of decomposition in water, release fatty and oily byproducts which will produce an oily sheen on the water.

The analytical method for oil and grease (detection limit 1.0 $mg \cdot L^{-1}$) gives only a gross estimate of the amount present. This particular method does not identify individual compounds.

Some organic chemicals can be absorbed from water through the skin, but until further research has been done, the possible risk to bathers cannot be evaluated.

2.6 REFERENCES

Anonymous. 1984. Water quality criteria; request for comments. Fed. Regist. 49: 21987-21988.

Anonymous. 1986. Bacteriological ambient water quality criteria; availability. Fed. Regist. 51: 8012-8016.

Appleby, A.G. 1986. Personal communication. Department of Parks and Renewable Resources, Regina, Saskatchewan.

Aziz, K.M.S. 1974. Diarrhea toxin obtained from a waterbloom-producing species, *Microcystis aeruginosa* Kutzing. Science 1[illegible] 1206-1207. (Cited in Health and Welfare Canada 1983.)

Barica, J. 1975. Collapses of algal blooms in prairie pothole lakes: their mechanism and ecological impacts. Verh. Int. Ver. Theor. Angew. Limnol. 19: 606-615.

Basu, P.K., M. Avaria, A. Cutz and M. Chipman. 1984. Ocular effects of water from acidic lakes: an experimental study. Can. J. Ophthalmol. 19: 134-141.

Berg, G. and T.G. Metcalf. 1978. Indicators of viruses in waters. *In* Indicators of Viruses in Water and Food. G. Berg (ed.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 267-296. (Cited in Health and Welfare Canada 1983.)

Brownlee, B. 1986. Personal communication. National Water Research Institute, Environment Canada, Burlington, Ontario.

Carmichael, W.W. 1986. Toxins of freshwater Cyanobacteria (blue-green algae). Abstract from 69th Canadian Chemical Conf., June 1-4, Saskatoon, Saskatchewan.

Dufour, A.P. 1977. *Escherichia coli*: The fecal coliform. *In* Bacterial Indicators/Health Hazards Associated with Water. A.W. Hoadley and B.J. Dutka (eds.). ASTM Spec. Tech. Publ. 635. American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 48-58. (Cited in Health and Welfare Canada 1983.)

Dufour, A.P. 1982. Fresh recreational water quality and swimming-associated illness. *In* Proc. 2nd Natl. Symp. on Municipal Wastewater Disinfection. U.S. EPA Health Effects Research Laboratory, Orlando, Florida. (Cited in IJC 1983.)

Dufour, A.P. 1984. Health Effects Criteria for Fresh Recreational Waters. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA 600/1-84/004.

Dutka, B.J. 1986. Personal communication. National Water Research Institute, Environment Canada, Burlington, Ontario.

Environment Canada. 1972. Guidelines for Water Quality Objectives and Standards. A Preliminary Report. Inland Waters Directorate, Ottawa. Tech. Bull. No. 67.

Erlandsen, S.L. and E.A. Meyer (eds.). 1984. *Giardia* and Giardiasis: Biology, Pathogenesis, and Epidemiology. Plenum Press, New York. 407 pp.

Federal Water Pollution Control Administration. 1968. Report of the National Technical Advisory Committee on Water Quality Criteria. U.S. Government Printing Office, Washington, D.C. (Cited in Health and Welfare Canada 1983.)

Geldreich, E.E. 1966. Sanitary Significance of Fecal Coliform in the Environment. Water Pollution Control Res. Ser. No. WP-20-3. Government Printing Office, Washington, D.C. (Cited in Health and Welfare Canada 1983.)

Greenberg, A.E., R.R. Trussell and L.S. Clesceri. 1985. Standard Methods for the Examination of Water and Wastewater. 16th edition. American Public Health Association, Washington, D.C. 1268 pp.

Health and Welfare Canada. 1979. Guidelines for Canadian Drinking Water Quality 1978. Supply and Services Canada, Ottawa. 76 pp.

Health and Welfare Canada. 1983. Guidelines for Canadian Recreational Water Quality. Federal-Provincial Advisory Committee on Environmental and Occupational Health, Ottawa.

Hoadley, A.W. 1977. Potential health hazards associated with *Pseudomonas aeruginosa* in water. *In* Bacterial Indicators/Health Hazards Associated with Water. A.W. Hoadley and B.J. Dutka (eds.). ASTM Spec. Tech. Publ. 635. American Society for Testing and Materials, Philadelphia, Pennsylvania. (Cited in McNeill 1985.)

IJC. 1977. New and Revised Great Lakes Water Quality Objectives. Vol. II. Report to the Governments of the United States and Canada. International Joint Commission, Windsor, Ontario.

IJC. 1983. Report of the Aquatic Ecosystem Objectives Committee. Annual Report of the Great Lakes Science Advisory Board, November. International Joint Commission, Windsor, Ontario. pp. 4-20.

Kott, Y., H. Ben-Ari and N. Betzer. 1978. Lagooned, secondary effluents as water source for extended agricultural purposes. Water Res. 12: 1101-1106. (Cited in U.S. EPA 1984.)

Kreider, M.B. 1964. Pathogenic effects of extreme cold. *In* Medical Climatology. S. Licht and E. Licht (eds.). New Haven, Connecticut. pp. 428-468. (Cited in Health and Welfare Canada 1983.)

Laird, M., E.J. Bower, T. Dick, R.D.P. Eaton, G. Faubert, R.S. Freeman, J.C. Holmes, E. Meerovitch, T. Scholten and M.D. Sutton. 1980. Intestinal Parasites of Man in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18128. 69 pp.

Leggatt, E.A. 1986. Personal communication. Ontario Ministry of the Environment, Toronto, Ontario.

McGovern, T. 1983. Is the water safe for swimming? Maine Environ News 10(4): 1, 7, 8.

McLeod, J.A. and G.S. Bondar. 1952. A case of suspected algal poisoning in Manitoba. Can. J. Public Health 43: 347-350. (Cited in Health and Welfare Canada 1983.)

McNeill, A.R. 1985. Microbiological Water Quality Criteria: A Review for Australia. Department of Resources and Energy, Australian Water Resources Council. Tech. Pap. No. 85. Australian Government Publishing Service, Canberra. 566 pp.

Moore, R.E. 1977. Toxins from blue-green algae. BioScience 27: 797-802. (Cited in Health and Welfare Canada 1983.)

NAS. 1977. Drinking Water and Health. Part 1. National Academy of Sciences, Washington, D.C.

Neil, J.H. 1975. *Cladophora* in the Great Lakes. H. Shear and D. Konasewich (eds.). International Joint Commission, Windsor, Ontario. 179 pp.

Nicholls, K.H., J.L. Beaver and R.H. Estabrook. 1980. Lakewide Odours in Ontario and New Hampshire Caused by *Chrysochromulina breviturrita* Nich. (Prymnesiophyceae). A.P.I.O.S. Tech. Rep. No. 001/81. Ontario Ministry of the Environment, Toronto, Ontario. 11 pp.

Nicholls, K.H., W. Kennedy and G. Hammett. 1980. A fish-kill in Heart Lake, Ontario, associated with the collapse of a massive population of *Ceratium hirundinella* (Dinophyceae). Freshwater Biol. 10: 553-561.

Palmer, C.M. 1962. Algae in Water Supplies. U.S. Public Health Service Publ. No. 657. Washington, D.C.

Prescott, G.W. 1948. Objectionable algae with reference to the killing of fish and other animals. Hydrobiologia 1: 1-13.

Rand, M.C., A.E. Greenberg and M.J. Taras (eds.). 1975. Standard Methods for the Examination of Water and Wastewaters. 14th edition. American Public Health Association, Washington, D.C. 1193 pp.

Reid, G.K. and R.D. Wood. 1976. Ecology of Inland Waters and Estuaries. 2nd edition. D. Van Nostrand Co., Toronto, Ontario. 485 pp.

Senior, V.E. 1960. Algal poisoning in Saskatchewan. Can. J. Comp. Med. 24: 26-31. (Cited in Health and Welfare Canada 1983.)

Seyfried, P.L. and R.J. Cook. 1984. Otitis externa infections related to *Pseudomonas aeruginosa* levels in five Ontario lakes. Can. J. Public Health 75: 83-91.

Singleton, H.J. 1986. Personal communication. British Columbia Ministry of Environment, Victoria, British Columbia.

Taft, C.E. 1965. Water and Algae, World Problems. Educational Publ., Chicago, Illinois.

Tobin, R.S. 1986. Personal communication. Health and Welfare Canada, Ottawa.

Toronto Area Watershed Management Strategy Steering Committee. 1985. Humber River Bacteriological Study. Tech. Rep. No. 6. Toronto, Ontario.

U.S. EPA. 1984. Drinking Water Microbiology. Committee on the Challenge of Modern Society (NATO/CCMS). NATO/CCMS Drinking Water Pilot Project Series CCMS 128. Office of Drinking Water, U.S. Environmental Protection Agency. EPA 570/9-84-006. 545 pp.

U.S. EPA. 1985. Test Methods for *Escherichia coli* and Enterococci in Water by the Membrane Filter Procedure. EPA Research and Development Rep. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA 600/4-85-076. 25 pp.

U.S. EPA. 1986. Bacteriological Ambient Water Quality Criteria for Marine and Fresh Recreational Waters. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-84-002.

Vlassoff, L.T. 1981. Personal communication. Ontario Ministry of the Environment, Toronto, Ontario. (Cited in Health and Welfare Canada 1983.)

Wheater, D.W.F., D.D. Mara and J. Oragui. 1979. Indicator systems to distinguish sewage from stormwater runoff and human from animal faecal material. *In* Biological Indicators of Water Quality. A. James and L. Evison (eds.). John Wiley and Sons, Chichester, England.

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3.0 FRESHWATER AQUATIC LIFE

3.1 INTRODUCTION

The freshwater ecosystem is composed of the biological community (producers, consumers, decomposers) and the physical and chemical (abiotic) components and their interactions. Diverse aquatic ecosystems exist within Canada and they are influenced by numerous factors.

Within the aquatic ecosystem a complex interaction of physical and biochemical cycles exists and changes do not occur in isolation. For example, the annual, as well as long-term, hydrographs of a river basin are a result of the basin's hydrological regime. Superimposed on these are the biochemical cycles such as the diurnal cycle, which is measured in terms of hours and the seasonal cycle, which is measured in terms of months. As a result, aquatic systems undergo constant change. However, an ecosystem has evolved over a long period of time and the organisms have become adapted to their environment. The system may be unbalanced by natural factors which include drastic climatic variations, or disease, or by factors due to human activity. Any changes, especially rapid ones, could have detrimental or disastrous effects.

Adverse effects due to human activity, such as the presence of toxic chemicals in industrial effluents, will affect many components of the aquatic biota, the magnitude of which will depend on both biotic and abiotic site-specific characteristics.

When developing and using guidelines for the protection of aquatic life, ideally there should be complete information on the parameter of concern. This should include: form and fate in the aquatic environment; quantitative exposure/effect relationships; and fate within organisms over a wide range of exposure concentrations. A relevant information base for a particular parameter is rarely complete and there are often many gaps in knowledge. Generally, the more information that is available on exposure/effect, the more reliable the guideline will be.

In order to use the scientific information in this chapter to recommend site-specific water quality objectives, the local water quality, resident biotic species, local water demands and other factors have to be considered (see Appendix IV). A number of agencies have developed their own guidelines which are appropriate to the local water type and needs. These documents and the information contained in this publication will be updated as the results of further research become available.

The Canadian guidelines for aquatic life are not restricted to a particular (biotic) species, but species-specific information is provided in the rationale so that authorities may determine the appropriateness of the guideline for the protection and enhancement of local species. The use of common test species as indicators (e.g. rainbow trout as an indicator of salmonid sensitivity) will often be necessary until data on native species are available.

In some cases, natural concentrations of a substance may exceed the guideline without any apparent effect on the biota. Usually this is because the substance is not present in a bioavailable form. It may also indicate that modifying factors are present at that location and the substance is not toxic under those conditions. For waters of superior quality, impairment to guideline concentrations should not be acceptable. Such considerations should form part of the rationale for site-specific water quality objectives. The natural concentrations of parameters and their range should also be taken into account in the design of monitoring programs and the interpretation of the resulting data.

When developing guidelines and site-specific objectives for aquatic life, the aquatic ecosystem should be viewed as a whole unit, not as isolated organisms affected by one (or a few) pollutant(s). The aquatic ecosystem is part of a complex system with aquatic and terrestrial components and should not be studied in isolation.

Table 3-1 summarizes the guidelines which are recommended for the protection of freshwater aquatic life. For information on each particular numerical limit, the reader is referred to those sections outlining the documents reviewed and the rationale used in developing the guidelines.

3.1.1 Procedure for the Development of Guidelines

Publications by the following agencies were consulted: Water Quality Branch of Environment Canada; Provincial and Territorial Departments; the International Joint Commission; the United States Environmental Protection Agency (U.S. EPA) and the European Inland Fisheries Advisory Commission (EIFAC). Additional recent research was consulted when it was thought to be critical for recommending a water quality guideline for the Canadian situation. Information on the sources, concentrations and fate of water quality parameters in the Canadian aquatic environment is outlined in Chapter 6.

3.1.1.1 Review of Guidelines

The first step of the procedure was to review existing guidelines to determine if they were appropriate to Canadian conditions. Guidelines were considered appropriate and, therefore, adopted if they were based on a recent review of sufficient literature and if they applied to Canadian conditions.

3.1.1.2 Modifications of Guidelines

If guidelines were available that were inappropriate to Canadian conditions, but data were available for their modification, then modifications were made and new guidelines prepared.

Water quality criteria of the U.S. Environmental Protection Agency and guidelines from other sources were considered because, in many cases, they were developed from the most recent and thorough review of the existing data base. Some existing guidelines were based on a number of decisions made by other administrations. For example, the U.S. EPA developed very stringent requirements defining an adequate data base (U.S. EPA 1985a). As a result, numerical limits for some water quality parameters were not established, even though a body of information existed. The decisions of the U.S. EPA were considered, but not always adopted.

Table 3-1. Summary – Guidelines for Freshwater Aquatic Life

Parameter	Guideline	Comments
Inorganic parameters		
Aluminum[1]	0.005 mg·L^{-1}	$pH<6.5$; $[Ca^{2+}]<4.0$ mg·L^{-1}; $DOC<2.0$ mg·L^{-1}
	0.1 mg·L^{-1}	$pH\geq6.5$; $[Ca^{2+}]\geq4.0$ mg·L^{-1}; $DOC\geq2.0$ mg·L^{-1}
Antimony	ID[2]	
Arsenic	0.05 mg·L^{-1}	
Beryllium	ID	
Cadmium	0.2 µg·L^{-1}	Hardness 0-60 mg·L^{-1} ($CaCO_3$)
	0.8 µg·L^{-1}	Hardness 60-120 mg·L^{-1} ($CaCO_3$)
	1.3 µg·L^{-1}	Hardness 120-180 mg·L^{-1} ($CaCO_3$)
	1.8 µg·L^{-1}	Hardness >180 mg·L^{-1} ($CaCO_3$)
Chlorine (total residual chlorine)	2.0 µg·L^{-1}	Measured by amperometric or equivalent method
Chromium	0.02 mg·L^{-1}	To protect fish
	2.0 µg·L^{-1}	To protect aquatic life, including zooplankton and phytoplankton
Copper	2 µg·L^{-1}	Hardness 0-60 mg·L^{-1} ($CaCO_3$)
	2 µg·L^{-1}	Hardness 60-120 mg·L^{-1} ($CaCO_3$)
	3 µg·L^{-1}	Hardness 120-180 mg·L^{-1} ($CaCO_3$)
	4 µg·L^{-1}	Hardness >180 mg·L^{-1} ($CaCO_3$)
Cyanide	5.0 µg·L^{-1}	Free cyanide as CN
Dissolved oxygen	6.0 mg·L^{-1}	Warm-water biota – early life stages
	5.0 mg·L^{-1}	– other life stages
	9.5 mg·L^{-1}	Cold-water biota – early life stages
	6.5 mg·L^{-1}	– other life stages
Iron	0.3 mg·L^{-1}	
Lead	1 µg·L^{-1}	Hardness 0-60 mg·L^{-1} ($CaCO_3$)
	2 µg·L^{-1}	Hardness 60-120 mg·L^{-1} ($CaCO_3$)
	4 µg·L^{-1}	Hardness 120-180 mg·L^{-1} ($CaCO_3$)
	7 µg·L^{-1}	Hardness >180 mg·L^{-1} ($CaCO_3$)
Mercury	0.1 µg·L^{-1}	
Nickel	25 µg·L^{-1}	Hardness 0-60 mg·L^{-1} ($CaCO_3$)
	65 µg·L^{-1}	Hardness 60-120 mg·L^{-1} ($CaCO_3$)
	110 µg·L^{-1}	Hardness 120-180 mg·L^{-1} ($CaCO_3$)
	150 µg·L^{-1}	Hardness >180 mg·L^{-1} ($CaCO_3$)
Nitrogen		
Ammonia (total)	2.2 mg·L^{-1}	pH 6.5; temperature 10°C (see Table 3-12)
	1.37 mg·L^{-1}	pH 8.0; temperature 10°C
Nitrite	0.06 mg·L^{-1}	
Nitrate		Concentrations that stimulate prolific weed growth should be avoided
Nitrosamines	ID	
pH	6.5-9.0	
Selenium	1 µg·L^{-1}	
Silver	0.1 µg·L^{-1}	
Thallium	ID	
Zinc[3]	0.03 mg·L^{-1}	
Organic parameters		
Acrolein	ID	
Aldrin/dieldrin	4 ng·L^{-1} (dieldrin)	

Table 3-1. (Cont'd)

Parameter	Guideline	Comments
Benzene[3]	0.3 mg·L^{-1}	
Chlordane	6 ng·L^{-1}	
Chlorinated benzenes[3]		
Monochlorobenzene	15 µg·L^{-1}	
Dichlorobenzene 1,2- and 1,3-	2.5 µg·L^{-1}	
1,4-	4.0 µg·L^{-1}	
Trichlorobenzene 1,2,3-	0.9 µg·L^{-1}	
1,2,4-	0.5 µg·L^{-1}	
1,3,5-	0.65 µg·L^{-1}	
Tetrachlorobenzene 1,2,3,4-	0.10 µg·L^{-1}	
1,2,3,5-	0.10 µg·L^{-1}	
1,2,4,5-	0.15 µg·L^{-1}	
Pentachlorobenzene	0.030 µg·L^{-1}	
Hexachlorobenzene	0.0065 µg·L^{-1}	
Chlorinated ethylenes[3]		
Tetrachloroethylene	260 µg·L^{-1}	
Di- and trichloroethylenes	ID	
Chlorinated phenols		
Monochlorophenols	7 µg·L^{-1}	
Dichlorophenols	0.2 µg·L^{-1}	
Trichlorophenols	18 µg·L^{-1}	
Tetrachlorophenols	1 µg·L^{-1}	
Pentachlorophenol	0.5 µg·L^{-1}	
DDT	1 ng·L^{-1}	
Dinitrotoluenes	ID	
Diphenylhydrazine	ID	
Endosulfan	0.02 µg·L^{-1}	
Endrin	2.3 ng·L^{-1}	
Ethylbenzene[3]	0.7 mg·L^{-1}	
Halogenated ethers	ID	
Heptachlor + Heptachlor epoxide	0.01 µg·L^{-1}	
Hexachlorobutadiene	0.1 µg·L^{-1}	
Hexachlorocyclohexane isomers	0.01 µg·L^{-1}	
Hexachlorocyclopentadiene	ID	
Phenols (total)	1 µg·L^{-1}	
Nitrobenzene	ID	
Nitrophenols	ID	
Phenoxy herbicides (2,4-D)	4.0 µg·L^{-1}	
Phthalate esters		
DBP	4 µg·L^{-1}	
DEHP	0.6 µg·L^{-1}	
Other phthalate esters	0.2 µg·L^{-1}	
Polychlorinated biphenyls (total)	1 ng·L^{-1}	
Polycyclic aromatic hydrocarbons	ID	

Table 3-1. (Cont'd)

Parameter	Guideline	Comments
Toluene	0.3 $mg \cdot L^{-1}$	
Toxaphene	8 $ng \cdot L^{-1}$	
Physical parameters		
Temperature		Thermal additions should not alter thermal stratification or turnover dates, exceed maximum weekly average temperatures, and exceed maximum short-term temperatures (see Section 3.2.3.1.1)
Total suspended solids	increase of 10.0 $mg \cdot L^{-1}$	Background suspended solids ≤ 100.0 $mg \cdot L^{-1}$
	increase of 10% above background	Background suspended solids >100.0 $mg \cdot L^{-1}$

[1] Concentrations of heavy metals reported as total metal in an unfiltered sample.
[2] ID = insufficient data to recommend a guideline.
[3] Tentative guideline.

The following modifications were decided upon:

1. In setting the Canadian guidelines, all components of the aquatic ecosystem (e.g. phytoplankton, zooplankton, benthos, macrophytes, fish) were considered insofar as data were available. When data were limited, tentative guidelines were deemed preferable to no guidelines. Tentative Canadian guidelines were developed if the data base contained, as a minimum, acute toxicity data for several species of fish, including salmonids, and several species of invertebrates, even though the need for more data was recognized.
2. The approach to the development of guidelines for aquatic life of the International Joint Commission Water Quality Board (IJC 1975) and the Ontario Ministry of the Environment (1979) was generally adopted. This approach states that the guidelines "are set at such values as to protect all forms of aquatic life and all aspects of the aquatic life cycles. The clear intention is to protect all life stages during indefinite exposure to the water." This approach contrasts with the U.S. EPA approach in which "protection of all species at all times and places is not deemed necessary" (U.S. EPA 1985a). For the Canadian guidelines, the Ontario approach was modified to the extent that outlying values were not considered if they were based on a single unsubstantiated value or a nonstandard test, or the species in question is not prevalent in Canada.
3. The two-number approach introduced by the U.S. EPA in 1980 (Anonymous 1980), consisting of a maximum and an average number, was not adopted because of the lack of a generally accepted and scientifically sound basis for the duration of the averaging period.

   Between 1980 and 1985, the U.S. EPA considered averaging periods of 24 h, 4 d and 30 d. Recent studies have shown that average concentrations obtained from chronic laboratory tests cannot be applied to field situations, because unvarying concentrations are considered to be less toxic than fluctuating concentrations even though the average may be the same (U.S. EPA 1985a). In Canada, monitoring frequency is seldom adequate to support 24-h or 4-d average guidelines. As a consequence, an average guideline would seldom be directly applicable. A single maximum value was adopted for the Canadian guidelines.

   The maximum value is based on a long-term "no-effect" concentration rather than on an acute concentration for the following reasons. If the guidelines were closer to the acute concentration, a concentration in the water continuously just below such a guideline could cause chronic effects and eventually harm or eliminate a resident population. The assumption that a single (often monthly) sample always represents an isolated instantaneous condition places the aquatic environment at risk, because the condition may continue for hours, days or even weeks. Because the laboratory turn-around time for some monitoring can be long, the guidelines for aquatic life are more useful if set at "preventive" rather than "emergency" levels.
4. A consistent approach to the development of guidelines was considered desirable, but variation in the amount and type of data available sometimes necessitated modification of such an approach. The guidelines were generally derived from the most sensitive of the following: "no negative effect" data obtained from life-cycle or early-life-stage tests of chronic toxicity; thresholds for the tainting of fish flesh; or concentrations in the water which would result in acceptable concentrations in the edible portions of marketable fish (or the protection of natural consumers). The guidelines were compared to known chronic toxicity values, and modifications were made to the guidelines to provide long-term protection of important sensitive plant and animal species or their uses, if necessary. When a guideline is needed, but sufficient chronic toxicity data are not available, short-term toxicity data multiplied by an "application factor" were used as a second choice.

   The application factors are: 0.05 of the 96-h LC_{50} of the most sensitive species for materials that are nonpersistent or have noncumulative effects; and 0.01 of the 96-h LC_{50} of the most sensitive species for materials that require additional caution because data are extremely limited. These numbers were derived from the Ontario Ministry of Environment (1979) application factors of 0.05 and 0.01, for nonpersistent and persistent effects respectively.

   If acute:chronic ratios were adequate, the application factor was modified to incorporate them by making it equal to 0.2 times the ratio. For all substances known to cause harmful effects as a result of biomagnification, bioaccumulation factors were taken into account in the calculation of the guideline.

The geometric mean of all acute toxicity values for the most sensitive species was used. If the most sensitive species has a very limited geographic range or ecological role, the LC$_{50}$ value is deemed questionable, or the LC$_{50}$ is not substantiated by other data, a more representative species was chosen with an accompanying explanation in the rationale. If toxicity is related to water hardness, the U.S. EPA (1985a) formula was used either directly or in a slightly modified form. The method used to derive each guideline is described in the rationale.

5. The concept of "frequency of excess concentrations (average recurrence interval)" recently introduced by the U.S. EPA (1985a) was not incorporated into the Canadian guidelines. Although natural variability should be considered in the design of a monitoring program, the condition of allowing concentrations of a toxic substance to exceed a numerical limit by an unspecified amount (and therefore an unlimited amount) every 3 years on average should not be a condition to strive for. It could place a fish population in a perpetual state of recovery rather than allowing it to recover. The return period of 3 years was selected by the U.S. EPA (1985a) because "most aquatic ecosystems can probably recover from most excess concentrations in about three years." Documented studies of recoveries are few, and the abilities of ecosystems to recover differ greatly; both points were acknowledged by the U.S. EPA (1985a). Caution should also be used when applying the concept of recurrence interval, commonly used for natural events such as rainfall, to chemicals entering the aquatic environment from anthropogenic sources.
6. The analysis of the total element, or substance, in an unfiltered sample was adopted when appropriate. In general, this has been the approach taken in existing water quality guidelines used in Canada. It is protective of the environment because it measures the total quantity of the substance that is present. For example, substances adsorbed on suspended particles could be transported and later dissolved under different environmental conditions. Water quality criteria developed by the U.S. EPA are often based on the total recoverable method of analysis. The U.S. EPA has recently recommended an acid-soluble method, although the method has not yet been approved. The U.S. EPA believes that the analytical results obtained with the acid-soluble method more closely approximate the concentrations used in toxicity tests, as well as the fraction of the element that is considered to be bioavailable. Both approaches have advantages, and there is a lack of consensus on the "best" method at the present time (U.S. EPA 1985a).

3.1.1.3 Inappropriate or Inadequate Existing Guidelines

If guidelines for some parameters were available, but were deemed inappropriate to Canadian conditions, and no data were available for their modification, guidelines were not provided for those parameters. The need for further research was then identified. A review of existing information is included in the guidelines with an accompanying statement that guidelines could not be recommended.

3.2 GUIDELINES FOR THE PROTECTION OF FRESHWATER AQUATIC LIFE

3.2.1 Inorganic Parameters

3.2.1.1 Aluminum

3.2.1.1.1 Guideline (Tentative)

The concentration of total aluminum should not exceed 0.005 mg·L^{-1} in waters with a pH equal to or below 6.5. The concentration of total aluminum should not exceed 0.1 mg·L^{-1} in waters with a pH greater than 6.5.

3.2.1.1.2 Summary of Documents

The U.S. EPA (1973) recommended that apparent toxicity should be carefully examined in situations where the presence of ionic aluminum is suspected. Aluminum may have considerably greater toxicity than has been assumed. The U.S. EPA has not included aluminum in more recent criteria documents. No Canadian guidelines for aluminum pertaining to aquatic life were found, although the IJC (1975) proposed a numerical limit of 0.1 mg·L^{-1}. The Ontario Ministry of the Environment (1984) stated that concentrations of 0.1 mg·L^{-1} or greater would be deleterious to growth and survival of fish. Ontario is currently preparing numerical limits for aluminum (Ralston 1986).

3.2.1.1.3 Rationale

The toxicity of aluminum in fresh water has been reviewed by Burrows (1977) and Odonnell *et al.* (1984). The importance of pH has been investigated only recently, and significant gaps in knowledge remain.

In acidic waters, aluminum is generally more toxic over the pH range 4.4-5.4, with maximum toxicity occurring around pH 5.0-5.2, especially when the aluminum is in a supersaturated form (Schofield and Trojnar 1980). Aluminum can be acutely toxic to white sucker fry (*Catostomus commersoni*); a 50% mortality occurred at concentrations as low as 0.05 mg·L^{-1} at pH 5 (Driscoll *et al.* 1980). Threshold mortality of sucker fry (7-13% mortality) was observed by Baker and Schofield (1982) at an aluminum concentration of 0.01 mg·L^{-1} and pH 4.5-4.8.

Early developmental stages of salmonids also appear to be sensitive. Sac fry of lake trout (*Salvelinus namaycush*) exhibited 25% mortality at an aluminum concentration of 0.07 mg·L^{-1} and pH 4.6-5.6 (Gunn and Keller 1984). A 27% mortality of cleavage embryos of rainbow trout (*Salmo gairdneri* Richardson) occurred at a concentration of less than 0.02 mg·L^{-1} and pH 4.5 (Holtze 1983), and a 90% mortality in 4- to 8-d rainbow trout occurred at a concentration of 0.075 mg·L^{-1} (Neville 1985). The 96-h LC$_{50}$ for rainbow trout alevins was 0.12 mg·L^{-1} at pH 4.5 (Holtze 1983). The toxicity of aluminum is greatly reduced at circumneutral pH values.

Under very acidic conditions, the toxic effects of the high hydrogen ion concentration are more important than is the presence of low concentrations of aluminum. Aluminum has actually been shown to mitigate the effects of low pH (4.2-4.8) for certain aquatic life stages (Schofield and Trojnar 1980; Baker and Schofield 1982).

Under alkaline conditions, aluminum toxicity to fish also increases. Experiments using rainbow trout fingerlings held under basic conditions showed that the toxicity of dissolved aluminum was more severe, but suspended aluminum was also toxic (Freeman and Everhart 1971). A concentration of 0.52 mg·L^{-1} (total aluminum) produced 44% mortality after 45 d at pH 9. Complexing agents also affect the availability of aluminum to fish. The addition of fluoride, citrate and organic ligands such as humic acids all reduce the availability.

Physiological differences between fish from variation in species or life stage can modify the toxicity of aluminum (Odonnell *et al.* 1984). Toxicity of aluminum generally declines with age except under low pH (<4.4) conditions (Baker and Schofield 1982). Certain strains of fish exhibit tolerance to the stress of acidic waters; this variation in tolerance may be related to differences in the reaction to aluminum.

The toxicity of aluminum to aquatic organisms other than fish has been investigated recently. A 37% mortality occurred in the chironomid *Tanytarsus dissimilis* (second and third instars) after 55 d at an aluminum concentration of 0.8 mg·L^{-1} and pH 6.8 (Lamb and Bailey 1981). Fourth instar dipteran larvae, *Chaoborus punctipennis* and *Chironomus anthrocinus*, showed no increase in mortality at a concentration of 1 mg·L^{-1} and pH 3.5-6.5; however, the cladocerans *Daphnia catawba* and *Holopedium gibberum* had a 20-35% increase in mortality over controls at the same concentration and pH 4-5 (Havas and Likens 1985). The 48-h LC_{50} for *Ceriodaphnia* occurred at a concentration of 0.3-0.5 mg·L^{-1} and pH 5.5-6.0 (Shephard 1983). At an aluminum concentration of 0.68 mg·L^{-1}, *Daphnia magna* showed a 50% reproductive impairment after 3 weeks at pH 6.5-7.5 (Schofield and Trojnar 1980).

Amphibians are also susceptible to aluminum toxicity. American toad (*Bufo americanus*) egg hatching success was reduced from 75% (for controls at pH 4.3) to 56% with the addition of 0.01 mg·L^{-1} aluminum. The level of no significant effect was 0.005 mg·L^{-1} (Clark and LaZerte 1985).

Aquatic plants appear to be less sensitive than some invertebrates. A 50% reduction in root growth of eurasian milfoil (*Myriophyllum spicatum* L.) was observed at a concentration of 2.5 mg·L^{-1} and a circumneutral pH (Stanley 1974).

Tentative recommendations for aluminum are proposed because more literature has become available recently, especially for the pH range of 4.5-5.5. The guideline is divided into two parts based on Neville's (1985) observation that the physiological response of juvenile rainbow trout to 75 μg·L^{-1} aluminum is severe at pH 6.1, but minimal at pH 6.5. The numerical limit of 0.1 mg·L^{-1} first proposed by the U.S. EPA is tentatively recommended for waters with a pH equal to or greater than 6.5 (U.S. EPA 1973). For acidic waters with a pH equal to or below 6.5 a guideline of 0.005 mg·L^{-1} is recommended based on the no-effect concentration for the toad *Bufo americanus* (Clark and LaZerte 1985). The presence of calcium, dissolved organic carbon and possibly other complexing ligands may reduce the toxicity of aluminum, but the guideline cannot take these relationships into account until further data are available.

3.2.1.2 Antimony

3.2.1.2.1 Guideline

There are insufficient data to recommend a guideline for antimony.

3.2.1.2.2 Summary of Documents

The U.S. EPA (1980a) prepared a document on ambient water quality criteria for antimony, but insufficient data were available to establish a numerical limit. No other guidelines for antimony pertaining to aquatic life were found.

3.2.1.2.3 Rationale

Aquatic plants may be more sensitive to antimony than are fish or invertebrate species. Inhibition of chlorophyll *a* and reduction of cell numbers occur in the alga *Selenastrum capricornutum* at 610 and 630 μg·L^{-1}, respectively (U.S. EPA 1980a).

The available data for antimony indicate that acute and chronic toxicity to freshwater animal life occur at concentrations as low as 9 and 1.6 mg·L^{-1}, respectively (U.S. EPA 1980a). The acute toxicity of the soluble forms of antimony has been determined only for the invertebrate *Daphnia magna*; the lowest recorded toxicity occurred at 9 mg·L^{-1}. Chronic toxicity values are available for antimony exposure of the fathead minnow (*Pimephales promelas*) and *Daphnia magna*; the minnow is the more sensitive species (U.S. EPA 1980a).

Bioconcentration data for antimony in the aquatic environment are limited. After 28 d of exposure to antimony trioxide, whole-body concentrations of antimony in bluegill (*Lepomis macrochirus*) were no greater than concentrations in control fish (U.S. EPA 1980a).

3.2.1.3 Arsenic

3.2.1.3.1 Guideline

The concentration of total arsenic should not exceed 0.05 mg·L^{-1}.

3.2.1.3.2 Summary of Documents

Demayo *et al.* (1979a) and the IJC (1975) recommended 0.05 mg·L^{-1} for raw public water supplies, humans being more sensitive than aquatic life. Manitoba (Williamson 1983) recommended 0.05 mg·L^{-1} for raw water for domestic consumption and also for aquatic life. The Ontario Ministry of the Environment (1984) proposed a numerical limit of 0.10 mg·L^{-1} for aquatic life. This is currently being reviewed. The U.S. EPA (1976) did not establish a limit for arsenic to protect aquatic life. The U.S. EPA (1980b) recommended that the concentration of total recoverable trivalent inorganic arsenic not exceed 440 μg·L^{-1} at any time. The U.S. EPA (1980b) also stated that short-term effects on embryos and larvae of aquatic vertebrate species have been shown to occur at arsenic concentrations as low as 40 μg·L^{-1}.

The U.S. EPA (1985b) recommended that freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-d average concentration of arsenic(III) does not exceed 190 μg·L^{-1} more than once every 3 years on the average, and if the 1-h average concentration does not exceed

360 μg·L⁻¹ more than once every 3 years on the average. The U.S. EPA (1985b) considered that not enough data were available to derive numerical limits for inorganic arsenic(V) or organic arsenic compounds.

3.2.1.3.3 Rationale

There are several forms of arsenic in fresh water; the form is largely dependent upon the redox and pH levels in the water (Ferguson and Gavis 1972).

Invertebrates are generally more sensitive to arsenic than are adult fish. Acute toxicity of arsenic(III) to invertebrates occurred at concentrations that ranged upwards from two fairly similar values: 812 μg·L⁻¹ for a cladoceran (*Simocephalus serrulatus*) (Sanders and Cope 1966) and 874 μg·L⁻¹ for an amphipod (*Gammarus pseudolimnaeus*) (Call *et al.* 1983; Lima *et al.* 1984). The trivalent and pentavalent forms of arsenic appear to be similar in toxic potency. The lowest concentration of arsenic(V) causing acute toxicity was 850 μg·L⁻¹ for a cladoceran (*Bosmina longirostris*) (Passino and Novak 1984). The chronic toxicity of arsenic(III) is similar to the acute toxicity. Chronic toxicity to the cladoceran *Daphnia magna* occurred at a concentration of 914 μg·L⁻¹ arsenic (calculated from chronic limits of 630 and 1320 μg·L⁻¹) (Call *et al.* 1983; Lima *et al.* 1984). A 10% impairment of reproduction occurred at 302 μg·L⁻¹ arsenic(V) in *Daphnia magna* (Biesinger and Christensen 1972).

Concentrations of arsenic(III) causing an acute toxic response in fish ranged upwards from three fairly similar values: 13.34 mg·L⁻¹ for rainbow fingerling trout (*Salmo gairdneri*) (National Fisheries Research Laboratory 1980), 14.86 mg·L⁻¹ for the juvenile fathead minnow (*Pimephales promelas*) (Call *et al.* 1983; Lima *et al.* 1984) and 14.96 mg·L⁻¹ for adult brook trout (*Salvelinus fontinalis*) (Cardwell *et al.* 1976a). The lowest known acutely toxic concentration of arsenic(V) for fish is 10.8 mg·L⁻¹ for rainbow trout (Hale 1977).

The chronic toxicities of arsenic(III) and arsenic(V) to fish are in the same concentration range as acute toxicities to invertebrates. For example, chronic toxicities of these two forms to the fathead minnow occurred at 3.026 and 0.892 mg·L⁻¹, respectively (Call *et al.* 1983; Lima *et al.* 1984; U.S. EPA 1985b). The 28-d EC_{50} of arsenic(III) for embryos and larvae of rainbow trout was 550 μg·L⁻¹ (Birge *et al.* 1980). Physiological changes occurred in coho salmon parr-smolt (*Oncorhynchus kisutch*) after a 6-month exposure to 300 μg·L⁻¹ arsenic trioxide. These changes resulted in a less successful migration of the salmon (Nichols *et al.* 1984).

The lowest EC_{50} reported by the U.S. EPA (1985b) was 40 μg·L⁻¹ of arsenic(III) for embryos and larvae of the narrow-mouthed toad (*Gastrophryne carolinensis*), a species found in the southeastern U.S. (Birge 1978).

Higher water temperatures appear to increase the toxicity of arsenic, but water hardness does not. The median lethal time for green sunfish (*Lepomis cyanellus*) exposed to arsenic decreased when the water temperature increased (Sorenson 1976). Hardness did not affect the toxicity of inorganic arsenic(III) to the bluegill (*Lepomis macrochirus*) (Inglis and Davis 1972). Arsenicals are capable of counteracting the toxicity of selenium, but the action depends on the concentration of each parameter (Frost 1967).

Arsenic(V) appears to be more toxic to plants than is arsenic(III). Toxicity occurred at concentrations that ranged upwards from 48 μg·L⁻¹ for the alga *Scenedesmus obliquus* (Vocke *et al.* 1980).

Arsenic is not biomagnified, although it is concentrated from water by some aquatic organisms (Lunde 1970; Seydel 1972; Isensee *et al.* 1973). Lower forms of aquatic life may accumulate greater amounts of arsenic than do fish. The fish most likely to concentrate arsenic are bottom feeders (CPHA 1977).

The guideline of 0.05 mg·L⁻¹ as proposed by Demayo *et al.* (1979a) is recommended. It is well below concentrations that are known to be toxic to sensitive early life stages of fish. The data suggest that one algal species, *Scenedesmus obliquus*, may not be protected by continuous exposure to arsenic at a concentration of 0.05 mg·L⁻¹.

3.2.1.4 Beryllium

3.2.1.4.1 Guideline

There are insufficient data to recommend a guideline for beryllium. (See 3.1.1.1.)

3.2.1.4.2 Summary of Documents

The U.S. EPA (1976) established numerical limits for total recoverable beryllium of 11 and 1100 μg·L⁻¹ to protect aquatic life in soft and hard water, respectively. A later review (U.S. EPA 1980c) found that there were insufficient data to calculate final acute or chronic values. As a result, numerical limits were not recommended by the U.S. EPA in 1980.

The Province of Ontario (Ontario Ministry of the Environment 1984) has recommended concentrations of 0.011 and 1.10 mg·L⁻¹ for water hardnesses less than and greater than 75 mg·L⁻¹ as $CaCO_3$, respectively.

3.2.1.4.3 Rationale

The acute toxicity of beryllium to freshwater fish is related to water hardness, with beryllium being more toxic in soft water. Data are available for acute toxicity to the fathead minnow (*Pimephales promelas*), guppy (*Poecilia reticulata*) and bluegill (*Lepomis macrochirus*) over a hardness range of 20-400 mg·L⁻¹; within this range, acute toxicity decreased about two orders of magnitude with increasing hardness (U.S. EPA 1980c). In soft water, the sensitivities of the few species tested ranged over an order of magnitude; acutely toxic concentrations (from five bioassays) for the most sensitive species, the guppy, ranged from 130 to 450 μg·L⁻¹ (Slonim 1973) at a hardness of 23 mg·L⁻¹ (as $CaCO_3$). The sensitivity of the fathead minnow was very similar at a similar hardness; toxicity occurred at a concentration of 150 μg·L⁻¹ (Tarzwell and Henderson 1960).

The acute toxicity of beryllium to the only invertebrate species studied, *Daphnia magna*, was comparable to the acute toxicity to fish. No relationship is available for water hardness and toxicity of beryllium to invertebrate species. Beryllium was more toxic to salamanders (*Ambystoma* spp.) in soft water than in hard water (Slonim and Ray 1975); the toxicities fell within the same range as that for fish. Toxicity data for a green alga (*Chlorella vannielii*) indicate that it is resistant (Karlander and Krauss 1972).

No chronic tests with beryllium have been conducted on fish. There has been one chronic test with the invertebrate *Daphnia magna*; effects on reproduction occurred at 5.3 $\mu g \cdot L^{-1}$ (U.S. EPA 1980c).

Beryllium does not appear to biomagnify in freshwater ecosystems (Cowgill 1973).

3.2.1.5 Cadmium

3.2.1.5.1 Guideline

The concentration of total cadmium should not exceed those shown in Table 3-2. Some species of zooplankton may not be protected if continuously exposed to 0.2 $\mu g \cdot L^{-1}$ of cadmium in soft water.

Table 3-2. Recommended Guidelines for Total Cadmium for Waters of Different Hardness

Hardness ($mg \cdot L^{-1}$ as $CaCO_3$)		Concentration of cadmium ($\mu g \cdot L^{-1}$)
0-60	(soft)	0.2
60-120	(medium)	0.8
120-180	(hard)	1.3
>180	(very hard)	1.8

3.2.1.5.2 Summary of Documents

A concentration of total cadmium not exceeding 0.2 $\mu g \cdot L^{-1}$ has been recommended in Canada (IJC 1976; Reeder *et al.* 1979a; Ontario Ministry of the Environment 1984). The NRCC (1979a) summarized the effects of cadmium in the Canadian environment, although no numerical limits were recommended.

The U.S. EPA (1985c) has recently recommended the measurement of acid-soluble cadmium; however, the total recoverable method has been recommended for use until an acid-soluble method is approved. The U.S. EPA (1985c) established 4-d and 1-h numerical limits for total recoverable cadmium which may be exceeded once every 3 years on average. These limits are expressed as formulae requiring a value for water hardness. The 4-d averages are 0.66, 1.1 and 2.0 $\mu g \cdot L^{-1}$, and the 1-h averages are 1.8, 3.9 and 8.6 $\mu g \cdot L^{-1}$, at water hardnesses of 50, 100 and 200 $mg \cdot L^{-1}$ as $CaCO_3$, respectively.

The Province of Manitoba has established limits of 0.012, 0.025 and 0.051 $\mu g \cdot L^{-1}$ for waters with hardnesses of 50, 100 and 200 $mg \cdot L^{-1}$ as $CaCO_3$, respectively (Williamson 1983).

The tentative EIFAC guidelines to protect European fisheries (Alabaster and Lloyd 1982) are based on annual water quality data expressed as 50- and 95-percentile concentrations of soluble cadmium. The maximum concentrations are 0.05 and 0.1, respectively, of the median threshold concentration for survival, taking into account the effect of water hardness. Maximum values are available for two fish species (Table 3-3).

Table 3-3. Approximate Maximum Annual Percentile Concentrations of Soluble Cadmium for Rainbow Trout and Perch as Recommended by EIFAC

Water hardness ($mg \cdot L^{-1}$ as $CaCO_3$)	Maximum annual percentile concentrations ($\mu g \cdot L^{-1}$)			
	Rainbow trout		Perch	
	50	95	50	95
10	0.3	0.6	10	20
50	0.4	0.9	15	30
100	0.5	1.0	19	38
300	0.75	1.5	25	50

Source: Alabaster and Lloyd 1982.

3.2.1.5.3 Rationale

Acute toxicity of cadmium to animal species in 44 genera are available (U.S. EPA 1985c); they range upwards from 1.0 $\mu g \cdot L^{-1}$ for exposure of rainbow trout (*Salmo gairdneri*). The U.S. EPA (1985c) calculated a species mean acute toxicity concentration of 3.589 $\mu g \cdot L^{-1}$ at a hardness of 50 $mg \cdot L^{-1}$ for rainbow trout. Aquatic insects are less sensitive to cadmium than are zooplankton (Reeder *et al.* 1979a). Aquatic plants are affected by cadmium at concentrations as low as 2 $\mu g \cdot L^{-1}$. These values are in the same range as acute toxicity values for fish and invertebrates. Blue-green algae appear to be more sensitive than do other algae (Hart 1975).

The acute toxicity of cadmium to aquatic biota is affected by water hardness, pH, water temperature and the presence of organic compounds, selenium and mixtures of metals. The modifying effect of water hardness on acute toxicity has been demonstrated with five animal species. Acute toxicity is lowered by calcium but not by magnesium (Carroll *et al.* 1979). Dissolved organics have been shown to substantially lower the toxicity of cadmium to cladocerans but not to fish (Geisy *et al.* 1977). Zinc accentuates the toxicity of cadmium to the aquatic plants *Lemna* and *Salvinia*. Selenium has a protective effect against cadmium toxicity to aquatic animals and plants (Reeder *et al.* 1979a); however, it can increase the retention of the metal and alter its internal distribution. The chronic toxicity to fathead minnows (*Pimephales promelas*) of a trimetal mixture of cadmium, copper and zinc was more toxic than would have been predicted by summation of their separate toxicities (Eaton 1973).

Chronic toxicity values for cadmium exposure of 12 fish and 4 invertebrate species in 13 genera ranged from 0.15 $\mu g \cdot L^{-1}$ for *Daphnia magna* to 156 $\mu g \cdot L^{-1}$ for Atlantic salmon (*Salmo salar*) (U.S. EPA 1985c). Species mean chronic toxicity values for cadmium exposure of the cladocerans *Daphnia magna* and *Moina macrocopa* were both 0.2 $\mu g \cdot L^{-1}$, but the sensitivity of natural populations of cladocerans varies seasonally (Borgmann *et al.* 1980). Salmonids are generally the most sensitive of the fish species. As little as 1 $\mu g \cdot L^{-1}$ of cadmium in water altered the sex hormone metabolism and interfered with reproduction of brook trout (*Salvelinus fontinalis*) (Freeman and Sangalang 1976). The chronic toxicity values for cadmium exposure of brook trout (*Salvelinus fontinalis*) were in the 1-2 $\mu g \cdot L^{-1}$ range; values for coho salmon (*Oncorhynchus kisutch*) (Lake Superior) and chinook salmon (*Oncorhynchus tshawytscha*) were similar (Chapman 1975; Eaton *et al.* 1978). Hardness has been shown to affect chronic toxicity, cadmium being less toxic in hard water (Sauter *et al.* 1976).

Bioconcentration factors range from 164 to 4190 for invertebrates and from 3 to 2213 for fish (U.S. EPA 1985c). Usually fish accumulate smaller amounts of cadmium in muscle than in most other tissues and organs (Benoit *et al.* 1976; Sangalang and Freeman 1979). Fulvic and humic acids increase the uptake of cadmium by rainbow trout (Ramamoorthy and Blumhagen 1984). Cadmium is taken up in large amounts by aquatic plants, but very little evidence was found by Reeder *et al.* (1979a) for biomagnification. Accumulation by organisms in an artificial stream decreased with increasing trophic level (Selby *et al.* 1985).

The U.S. EPA (1985c) formula:

$$\text{Cd conc.} = e^{(0.7852[\ln(\text{hardness})] - 3.490)}\ \mu g{\cdot}L^{-1}$$

has been used to calculate numerical limits for different water hardnesses. The recommended guidelines in Table 3-2 were derived using the lowest hardness within each category; a hardness of 10 mg·L^{-1} was assumed for the soft-water category. The guidelines were based on the U.S. EPA formula for chronic rather than acute toxicity, because chronic data are available for cadmium exposure to a wide range of species, the acute:chronic ratios are scattered and do not follow a consistent pattern, and the slope of the curve for toxicity versus water hardness is slightly different for the chronic data.

3.2.1.6 Chlorine

3.2.1.6.1 Guideline

The concentration of total residual chlorine, as measured by the amperometric (or equivalent) method, should not exceed 2.0 µg·L^{-1}.

3.2.1.6.2 Summary of Documents

A numerical limit of 2.0 µg·L^{-1} total residual chlorine has been recommended by the IJC (1978a) and Ontario Ministry of the Environment (1984). Manitoba has recommended a limit of 2.0 µg·L^{-1} for cold-water aquatic life and 0.01 mg·L^{-1} for cool-water aquatic life (Williamson 1983). All limits stipulate total chlorine as measured by the amperometric (or equivalent) method (CCREM 1985). For the protection of European freshwater fish, EIFAC recommended a maximum concentration of 4 µg·L^{-1} hypochloric acid (HOCl) (Alabaster and Lloyd 1982). The amount of total chlorine corresponding to this concentration varies according to temperature and pH. The corresponding concentration of total chlorine would equal 4 µg·L^{-1} at pH 6, 5 µg·L^{-1} at pH 7, 11-16 µg·L^{-1} at pH 8 and 75-121 µg·L^{-1} at pH 9. The lower and upper ranges represent water temperatures of 5 and 25°C, respectively.

The U.S. EPA (1976) proposed numerical limits of 2.0 µg·L^{-1} total residual chlorine for salmonid fish and 10.0 µg·L^{-1} for other freshwater organisms. These limits were replaced by the U.S. EPA in 1985. The new recommendations for freshwater aquatic organisms and their uses state that aquatic organisms should not be affected unacceptably if the 4-d average concentration of total residual chlorine does not exceed 11 µg·L^{-1} more than once every 3 years on the average, and if the 1-h average concentration does not exceed 19 µg·L^{-1} more than once every 3 years on the average (U.S. EPA 1985d).

3.2.1.6.3 Rationale

Fish and invertebrate species have similar ranges of sensitivity to chlorine. The U.S. EPA (1985d) summarized toxicity data for 33 species in 28 genera; the mean acute toxicity values ranged upwards from 28 µg·L^{-1} for chronic exposure of the cladoceran *Daphnia magna*. Data consistently indicated that *Daphnia magna* was the most sensitive species tested (Ward *et al.* 1976; Ward and DeGraeve 1980). The most sensitive fish were rainbow trout (*Salmo gairdneri*) fry and the pugnose shiner (*Notropis anogenus*); acute toxicity occurred at concentrations as low as 40 and 45 µg·L^{-1}, respectively (Wolf *et al.* 1975; Ward *et al.* 1976; Ward and DeGraeve 1978). However, mortality of salmon occurred in receiving streams with total residual chlorine concentrations as low as 20 µg·L^{-1} (Martens and Servizi 1974; Servizi and Martens 1974). Avoidance behaviour of rainbow trout was present, although slight, at a chlorine concentration of 1 µg·L^{-1}, and was stronger at 10 µg·L^{-1} under experimental conditions (Sprague and Drury 1969).

In general, the rate of lethality is rapid; nearly half the mortalities in a 96-h exposure occur in the first 12 h. Also, the concentrations that cause significant mortalities are only slightly higher than those that cause none. For example, the lowest concentration of total residual chlorine causing 100% mortality of coho salmon was only about three times the highest concentration that did not kill any coho salmon (*Oncorhynchus kisutch*) (Lamperti 1976).

The form of total residual chlorine affects the toxicity, at least in tests of short duration; free chlorine is more toxic than combined chlorine (Merkens 1958). Temperature has been frequently shown to affect toxicity under very short-term (i.e. a few hours) conditions; however, the results for the few 96-h tests that are available are less conclusive. Alkalinity does not affect the toxicity of chlorine, but many other factors such as pH, organic carbon and ammonia appear to (Larson *et al.* 1978; Fandrei and Collins 1979). The U.S. EPA (1985d) concluded, however, that no pattern was consistent or great enough to justify the dependence of numerical limits on any such factor.

Separate guidelines for warm-water and cold-water fish were recommended by Brungs (1973), but the distinction is no longer supported by additional data for warm-water fish species (Tsai 1973; Arthur *et al.* 1975; Bogaruds *et al.* 1976; Ward *et al.* 1976, 1977).

Chronic toxicity data are available for chlorine exposure of two invertebrate and one fish species; chronic toxicity concentrations ranged from less than 3.4 to 26 µg·L^{-1} (U.S. EPA 1985d). The lowest chronic toxicity concentrations for exposure of the invertebrates *Daphnia* sp. and *Gammarus pseudolimnaeus* were 3.7 and less than 3.4 µg·L^{-1}, respectively (Arthur and Eaton 1971; Arthur *et al.* 1975). In addition, one 7-d LC$_{50}$ for *Daphnia magna* was 2 µg·L^{-1} (Arthur *et al.* 1975). The lowest chronic toxicity concentration reported for life-cycle tests using the fathead minnow was 11.22 µg·L^{-1} (Arthur *et al.* 1975). A decrease in growth rate of juvenile coho salmon occurred at a chlorine concentration of 11 µg·L⁻¹ upon exposure for 21 d (Larson *et al.* 1977). There are few data comparing the relative chronic toxicities of different forms of chlorine.

Aquatic plants are less sensitive to chlorine than are fish and invertebrate species. Although there are substantial interspecies differences, diatoms tend to be more sensitive than green algae, which are generally more sensitive than blue-green algae. The EC_{50}s for phytoplankton communities from Lake Michigan ranged upwards from 160 µg·L⁻¹ (Brooks and Seegert 1977).

Total residual chlorine is not expected to bioaccumulate. Nevertheless, the reaction of these oxidants with organic substances may yield chlorinated organic compounds which may well bioaccumulate.

A guideline of 2.0 µg·L⁻¹ appears to protect aquatic life adequately. Recent data show that a division into warm-water and cold-water species is not warranted. The numerical limits of the U.S. EPA (1985d) are higher than the concentrations causing chronic toxicity in the two invertebrates tested, and equal to the concentration resulting in chronic toxicity in the fathead minnow, the only fish species for which a chronic value is available (U.S. EPA 1985d). Because the fathead minnow is less sensitive than many other fish species in acute tests, adoption of the U.S. EPA (1985d) limit is not recommended.

3.2.1.7 Chromium

3.2.1.7.1 Guideline

To protect fish, the concentration of total chromium should not exceed 0.02 mg·L⁻¹. To protect the aquatic community, including zooplankton and phytoplankton, the concentration of total chromium should not exceed 2.0 µg·L⁻¹.

3.2.1.7.2 Summary of Documents

A variety of numerical limits exist for chromium. Manitoba recommended 0.29 µg·L⁻¹ for chromium(VI) (Williamson 1983), and Ontario recommended 0.1 mg·L⁻¹ (total chromium) (Ontario Ministry of the Environment 1984). Taylor, Reeder and Demayo (1979) recommended a guideline of 0.04 mg·L⁻¹ (total chromium). The U.S. EPA (1976) limit of 0.1 mg·L⁻¹ was replaced by the U.S. EPA (1980d) value of 0.29 and 21 µg·L⁻¹ (total recoverable hexavalent chromium) as 24-h average maximum and instantaneous concentrations, respectively.

The U.S. EPA (1985e) recently established numerical limits for chromium(VI) based on 4-d and 1-h averages which may be exceeded once every 3 years on the average. These values are 11 and 16 µg·L⁻¹ as 4-d and 1-h averages, respectively.

The U.S. EPA (1985e) also established limits for chromium(III) based on 4-d and 1-h averages which may be exceeded once every 3 years on the average. These values are expressed as formulae requiring a value for water hardness. At water hardnesses of 50, 100 and 200 mg·L⁻¹ (as $CaCO_3$), the maximum 4-d average concentrations of chromium(III) are 120, 210 and 370 µg·L⁻¹, respectively, and the maximum 1-h average concentrations are 980, 1700 and 3100 µg·L⁻¹, respectively. The U.S. EPA (1985e) recommended measurement of acid-soluble chromium; however, the total recoverable method has been recommended until an acid-soluble method is approved.

3.2.1.7.3 Rationale

The U.S. EPA (1985e) compiled toxicity data related to chromium(VI) for a wide variety of animal species in 27 genera. Acute toxicities (96-h LC_{50}s) ranged upwards from 15.3 µg·L⁻¹ for exposure of the cladoceran, *Daphnia magna* (Call *et al.* 1981). All five tested species of daphnids (*Daphnia* sp., *Ceriodaphnia* sp.) were especially sensitive (Call *et al.* 1981; Mount and Norberg 1984; U.S. EPA 1985e). The species mean acute toxicity value for exposure of *Daphnia magna* was 23.07 µg·L⁻¹; the species mean acute toxicities for exposure of the most sensitive fish species were three orders of magnitude higher (U.S. EPA 1985e).

Acute toxicity of chromium(VI) appears to decrease as hardness and pH increase, but the available data were insufficient for the U.S. EPA (1985e) to develop numerical limits on the basis of water hardness.

Benoit (1976) found that the concentration of chromium(VI) causing toxicity to the early life stages of rainbow trout (*Salmo gairdneri*), 264.6 µg·L⁻¹, was the same as the concentration for chronic toxicity in the life-cycle test of the brook trout (*Salvelinus fontinalis*). The value for the fathead minnow (*Pimephales promelas*) is much higher (Pickering 1980). In all three chronic tests, a temporary reduction in growth occurred at low concentrations. In an early-life-stage test with rainbow trout, Sauter *et al.* (1976) determined a chronic value of 73.18 µg·L⁻¹ based on reduction in growth 60 d after hatch. Growth of chinook salmon (*Oncorhynchus tshawytscha*) was reduced at a measured concentration of 16 µg·L⁻¹ (Olson and Foster 1956). Daphnids are more sensitive; six chronic tests with five species of daphnids yielded toxicities at less than 2.5-40 µg·L⁻¹ (Trabalka and Gehrs 1977; U.S. EPA 1985e). A 7-d LC_{50} of 30 µg·L⁻¹ was reported for the young stages of the narrow-mouthed toad (*Gastrophryne carolinensis*) (Birge 1978).

Data on acute toxicity of chromium(III) are available for 20 freshwater animal species in 18 genera. Values (96-h LC_{50}s) range upwards from 2221 µg·L⁻¹ for the mayfly (*Ephemerella subvaria*). A concentration of 68.63 µg·L⁻¹ is available for chronic exposure of rainbow trout. Life-cycle tests with *Daphnia magna* in soft water yielded chronic toxicity concentrations of chromium(III) which ranged from 66 to 445 µg·L⁻¹ (U.S. EPA 1985e).

Water hardness has a significant effect on toxicity; chromium(III) is more toxic in soft water. The sensitivities of fish and invertebrates are comparable in soft water (U.S. EPA 1985e).

Phytoplankton have been shown to be more sensitive to chromium than are fish (Strik *et al.* 1975). Toxic concentrations of chromium(VI) range upwards from 2 µg·L⁻¹ for the blue-green alga, *Microcystis aeruginosa* (Bringmann 1975; Bringmann and Kuhn 1976, 1978a, b). Chromium(III) was less toxic than chromium(VI) to the green alga, *Selenastrum capricornutum* (U.S. EPA 1985e). Photosynthesis in natural populations of river algae (*Chlorella pyrenoidosa*, *Chlamydomonas reinhardii*) was inhibited at concentrations of chromium(VI) of 20 µg·L⁻¹ (Zaralonetis and Hampton 1974).

The three bioconcentration factors obtained for chromium(VI) exposure of rainbow trout were all less than 3 (Fromm and Stokes 1962; Buhler *et al.* 1977; Calamari *et al.* 1982). Algae accumulated chromium to a much greater extent; the bioconcentration factor for an algal community was 8500 (Patrick *et al.* 1975). The bioconcentration of chromium(III) has not been studied.

Based on a maximum acceptable toxicant concentration of 0.105 mg·L^{-1} for rainbow trout (Sauter *et al.* 1976) and a safety factor of 0.2 (Taylor, Reeder and Demayo 1979), a guideline of 0.02 mg·L^{-1} of total chromium would protect fish. This guideline was suggested by Taylor, Reeder and Demayo (1979) in a footnote, as the paper by Sauter *et al.* was received after the guideline had been written. A guideline at this level would not, however, protect many zooplankton or some phytoplankton.

Chronic toxicities for chromium exposure of five species of daphnids range upwards from less than 2.5 µg·L^{-1} (Trabalka and Gehrs 1977). Using these data, the U.S. EPA (1985e) calculated an acute:chronic ratio for daphnids of 2.917. The Canadian guideline was derived by dividing 23.07 µg·L^{-1}, the species mean acute value for the most sensitive species (*Daphnia magna*), by the acute:chronic ratio and multiplying by a safety factor of 0.2. The species mean acute value (derived from flow-through tests in which the concentration was measured) was supported by results for chromium exposure of four other species of cladocerans (U.S. EPA 1985e). Although this guideline is much lower than the guideline for fish, an examination of the literature indicates that cladocerans, which form an important component of the zooplankton, would not be protected by guidelines based on fish toxicity alone.

3.2.1.8 Copper

3.2.1.8.1 Guideline

The concentration of total copper should not exceed those shown in Table 3-4.

3.2.1.8.2 Summary of Documents

Demayo and Taylor (1981) recommended a guideline of 2.0 µg·L^{-1} total copper to protect aquatic life and wildlife. The IJC (1978b) and the Ontario Ministry of the Environment (1984) recommended 5.0 µg·L^{-1}; Manitoba recommended 5.6 µg·L^{-1} (Williamson 1983).

The NRCC published a summary of the behaviour of copper in the aquatic environment, including its toxicology (Spear and Pierce 1979). Although it does not recommend numerical limits, the NRCC document summarizes the data relevant to Canadian waters; it also contains formulae relating acute toxicity to water hardness and taxonomic group. Thus, knowing the taxonomic group and the water hardness, one can estimate the 96-h LC$_{50}$ of a fish species.

The numerical limit proposed by the U.S. EPA (1976) for copper was 0.1 times a 96-h LC$_{50}$ as determined through nonaerated bioassay using a sensitive aquatic resident species. In 1980, this value was replaced by a limit for total recoverable copper of 5.6 µg·L^{-1} as a 24-h average, and a hardness-related limit for a single sample given by the following formula:

$$\text{Cu conc.} = e^{(0.94[\ln(\text{hardness})] - 1.23)}\ \mu\text{g}\cdot\text{L}^{-1}$$

Table 3-4. Recommended Guidelines for Total Copper for Waters of Different Hardness

Hardness (mg·L^{-1} as CaCO$_3$)		Concentration of copper (µg·L^{-1})
0-60	(soft)	2
60-120	(medium)	2
120-180	(hard)	4
>180	(very hard)	6

Table 3-5. Approximate Maximum Annual Percentile Concentrations of Soluble Copper for Rainbow Trout as Recommended by EIFAC

Water hardness (mg·L^{-1} as CaCO$_3$)	Maximum annual percentile concentrations (µg·L^{-1})	
	50	95
10	1.0	5.0
50	6.0	22.0
100	10.0	40.0
300	28.0	112.0

Source: Alabaster and Lloyd 1982.

The most recent U.S. revision (U.S. EPA 1985f) established 4-d and 24-h numerical limits which may be exceeded once every 3 years on the average. These values are also expressed as formulae requiring a value for water hardness. The U.S. EPA (1985f) recommended analysis of acid-soluble copper, but use of total recoverable copper was recommended until an approved method for analysis of acid-soluble copper could be developed. At hardnesses of 50, 100 and 200 mg·L^{-1} as CaCO$_3$, the 4-d averages for copper were 6.5, 12 and 21 µg·L^{-1}, respectively, and the 1-h averages for copper were 9.2, 18 and 34 µg·L^{-1}, respectively.

To protect European freshwater fisheries, EIFAC has proposed numerical limits expressed as the 50- and 95-percentile concentrations of soluble copper. These are 0.05 and 0.2 of the threshold LC$_{50}$, respectively, taking into consideration the hardness of the water. The limits for rainbow trout shown in Table 3-5 may be applicable to other salmonid species. These values could be increased up to threefold if organic matter is present (Alabaster and Lloyd 1982).

3.2.1.8.3 Rationale

Acute toxicity data are available for species in 41 genera (U.S. EPA 1985f). At a water hardness of 50 mg·L^{-1}, the genera range in sensitivity to copper between 16.74 and 10 240 µg·L^{-1}. The lowest acute toxicity concentration for a single test was 6.5 µg·L^{-1} for exposure of the cladoceran *Daphnia magna* in hard water.

Toxicity is increased by decreases in water hardness and dissolved oxygen, and decreased in the presence of chelating agents, humic acids, amino acids and suspended solids (Alabaster and Lloyd 1982). The U.S. EPA (1985f) compiled data for eight species which indicated that acute toxicity decreases as hardness increases. Both calcium and magnesium increase tolerance at all trophic levels. Toxicity also decreases with increases in alkalinity (Spear and Pierce 1979).

The toxicity of copper in natural waters containing organic matter is less than that predicted from laboratory tests (Alabaster and Lloyd 1982). For example, the presence of sewage ameliorated the toxicity of copper. Guidelines should be adjusted upwards for surface waters with total organic carbon (TOC) concentrations significantly above 2-3 mg·L^{-1} (U.S. EPA 1985f).

Chronic toxicity data are available for 5 invertebrate and 10 fish species (U.S. EPA 1985f). The values range from 3.873 µg·L^{-1} in an early-life-stage test with brook trout (*Salvelinus fontinalis*) (Sauter *et al.* 1976) to 60.36 µg·L^{-1} in an early-life-stage test with northern pike (*Esox lucius*) (McKim *et al.* 1978). Values for invertebrate species lie within or slightly above this range (Nebeker *et al.* 1984). Larger rainbow trout (*Salmo gairdneri*) are approximately 2.5-3 times more resistant to copper than are juveniles (Chakoumakos *et al.* 1979). A similar size effect has been shown for the bluegill (*Lepomis macrochirus*) and guppy (*Lebistes reticulatus* Peter) (Tsai and Chang 1981, 1984).

Under laboratory conditions, changes in fish behaviour have been demonstrated at copper concentrations as low as 4.3 µg·L^{-1}. Fish may avoid copper, be attracted to it or orientate towards the source in a gradient of copper (Spear and Pierce 1979).

Embryo-larval stages of the leopard frog (*Rana pipiens*) were more sensitive to copper than rainbow trout embryos and alevins. The 4-d post-hatch LC_{50} for the leopard frog was 60 µg·L^{-1} compared to 110 µg·L^{-1} for rainbow trout (Birge and Black 1979).

Comparisons of the effect of daily pulses of copper compared with continuous exposure showed that the survival of the test organisms, rainbow trout and *Daphnia pulex*, decreased when they were exposed to the pulses at near-lethal concentrations, even though the average concentration was below the "no-effect" concentration in both cases (U.S. EPA 1985f).

The toxicity of copper under natural conditions cannot, in general, be predicted from extrapolated laboratory studies, as there are many modifying factors acting on the metal and on the exposed aquatic organisms. For example, increased dietary carbohydrate can significantly increase the chronic toxicity of copper to trout, and that impact is enhanced by reduced water temperature (Dixon and Hilton 1985).

Although chronic toxicity appears to decrease as water hardness increases, not all data show this trend consistently (Winner 1984). Both humic acid and selenium decrease the chronic toxicity of copper to the cladoceran *Daphnia pulex* (Winner 1984). In soft water, the presence of humic acid is a major factor modifying the tolerance of fish for copper.

Copper was shown to be toxic in mixtures of metals at concentrations below that which would be toxic if copper were acting alone in the water (Demayo and Taylor 1981). The toxicity of copper and zinc mixtures was shown to be more than additive by Anderson and Weber (1975), whereas a mixture of zinc, copper and nickel sulphates was shown to be additive in its toxicity to rainbow trout in soft water (Marking 1977).

The tolerance for copper of phytoplankton is generally comparable to the tolerance of fish. Copper concentrations ranging from 1 to 8000 µg·L^{-1} inhibited growth of plant species (U.S. EPA 1985f). Nitrogen fixation by blue-green algae was reduced by the addition of trace amounts of copper. There was a shift in community structure away from blue-green to green algae and diatoms by the addition of 5.0 µg·L^{-1} (Demayo and Taylor 1981). Acute toxicity tests with *Selenastrum capricornutum* also showed that toxicity decreases when the pH increases above 4 (Michnowicz and Weaks 1984). Algae from lakes in the Sudbury region, which have been affected by smelter fallout and tailings runoff, were more tolerant of copper than were algal strains from areas where the copper content of the water was very low. Rooted vascular plants are considered to be relatively tolerant of copper in water and sediments (Stokes 1975).

Bioconcentration factors of copper range from 0 for the bluegill to 2000 for the alga, *Chlorella regularis* (U.S. EPA 1985f). Copper concentrations in the edible portions of fish species are not high. There is a wide range in the amount of copper that can be accumulated by aquatic insects. Copper accumulates in algae to quite high levels (Demayo and Taylor 1981).

The guideline for soft water (i.e. 0-6 mg·L^{-1} as $CaCO_3$) (Table 3-4) is set equal to the guideline recommended by Demayo and Taylor (1981). The U.S. EPA (1985f) hardness formula for chronic toxicity (which was derived from a final acute value and an acute:chronic ratio) was used to derive the guideline for medium to very hard water:

$$\text{Cu conc.} = e^{(0.8545[\ln(\text{hardness})] - 1.465)}\ \mu\text{g}\cdot\text{L}^{-1}$$

Since the available information concerning the effect of hardness on the chronic toxicity of copper is inconclusive (U.S. EPA 1985f), the result from the formula was multiplied by an application factor of 0.2. The lowest hardness within each hardness category was used to calculate the values shown in Table 3-4.

3.2.1.9 Cyanide

3.2.1.9.1 Guideline

The concentration of free cyanide should not exceed 5.0 µg·L^{-1} as CN.

3.2.1.9.2 Summary of Documents

A recent detailed review of the effects of cyanides on aquatic organisms, especially fish, is available (Leduc *et al.* 1982). Manitoba (Williamson 1983) has recommended a limit of 3.5 µg·L^{-1}, whereas Ontario (Ontario Ministry of the Environment 1984) has recommended 5.0 µg·L^{-1}. Both limits are expressed as CN. British Columbia (Singleton 1986) recommended that (1) in a 30-d period the average concentration (based on a minimum of five weekly samples) of weak-acid-dissociable cyanide (expressed as CN) in unfiltered samples should not exceed 5 µg·L^{-1}; and (2) the maximum concentration should not exceed 10 µg·L^{-1} at any time. The numerical limit proposed by the IJC (1978a) for the Great Lakes is 5.0 µg·L^{-1} (free cyanide as CN).

The U.S. EPA (1976) proposed a limit of 5.0 µg·L^{-1}, but it was revised (U.S. EPA 1980e) to 3.5 µg·L^{-1} (free cyanide) as a 24-h average and to 52 µg·L^{-1} at any time. The most recent

U.S. EPA (1985g) document states that freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-d average concentration of cyanide does not exceed 5.2 $\mu g\cdot L^{-1}$ more than once every 3 years, on the average, and if the 1-h average concentration does not exceed 22 $\mu g\cdot L^{-1}$ more than once every 3 years, on the average. The U.S. EPA (1985g) recommends the measurement of free cyanide; however, until such a method has been approved, it is recommended that the numerical limits be applied using the total cyanide method.

3.2.1.9.3 Rationale

Data on the acute toxicity of free cyanide are available for a wide variety of freshwater species. (All data reported herein are for free cyanide as CN.) Most of the invertebrate species tested are much more tolerant than fish; all of the species tested thus far with acute sensitivities above an exposure concentration of 400 $\mu g\cdot L^{-1}$ are invertebrates (U.S. EPA 1985g). Two genera, *Daphnia* and *Gammarus*, are similar to fish in sensitivity (Dowden and Bennett 1965; Lee 1976; Cairns *et al.* 1978; Oseid and Smith 1979). Mean acute toxic concentrations for invertebrate species range from 95.6 to 2490 $\mu g\cdot L^{-1}$ (Cairns *et al.* 1978; Call *et al.* 1983). The toxic concentrations in one 48-h test using *Daphnia*, however, were 1, 180, 330 and 330 $\mu g\cdot L^{-1}$ at temperatures of 25, 15, 10 and 5°C, respectively (Cairns *et al.* 1978). The lowest chronic toxicity to an invertebrate occurred at a concentration of 18.33 $\mu g\cdot L^{-1}$ for a life-cycle test with the amphipod *Gammarus pseudolimnaeus* (Oseid and Smith 1979). There is a greater variability in the sensitivity of invertebrate species than of fish species.

Certain life stages and species of fish appear to be more sensitive to cyanide than others. Embryos, sac fry and warm-water species tended to be the most resistant. Free cyanide concentrations ranging from about 50 to 200 $\mu g\cdot L^{-1}$ eventually were fatal to juveniles of most of the more sensitive fish species; concentrations above 200 $\mu g\cdot L^{-1}$ became rapidly fatal to most juvenile fish (U.S. EPA 1985g). Many of the tests with fish were flow-through tests in which free cyanide was measured.

Of the 10 fish species tested, rainbow trout (*Salmo gairdneri*) is the most sensitive. The mean acute toxic concentration of cyanide for this species was 44.73 $\mu g\cdot L^{-1}$ (U.S. EPA 1985g). Individual acute toxic concentrations for exposure of rainbow trout have been observed as low as 27 $\mu g\cdot L^{-1}$. The highest cyanide concentration with no mortality to juvenile rainbow trout over 96 h was 17 $\mu g\cdot L^{-1}$ at 6°C (Kovacs 1979; Kovacs and Leduc 1982).

Field observations showed that brook trout (*Salvelinus fontinalis*) were affected by cyanide in minutes and could not be revived. Other species, such as yellow perch (*Perca flavescens*), white suckers (*Catostomus commersoni*), pumpkinseed sunfish (*Lepomis gibbosus*), rock bass (*Ambloplites rupestris*), burbot (*Lota lota*) and various species of minnows (Cyprinidae), reacted slowly and could be revived by placing them in clean water (Leduc *et al.* 1973; Leduc *et al.* 1982).

No pronounced relationship has been observed between the acute toxicity of cyanide to fish and alkalinity, hardness or pH below about 8.3 (U.S. EPA 1985g). There is little information on the effect of hardness, and most of it is contradictory (Leduc *et al.* 1982). Although pH has no appreciable effect on the toxicity of simple cyanides, such as HCN or CN^- in natural waters, small changes in pH will greatly modify the toxicity of metallocyanide complexes (Leduc *et al.* 1982). The maximum effect of pH (corresponding to a 10- to 13-fold increase in toxicity) on the tetracyanonickelate complex occurred at pH 7.4-7.8 (Doudoroff 1976).

Iron-cyanide complexes, on exposure to sunlight, dissociate to form hydrocyanic acid (HCN). In clear shallow waters, the natural removal of HCN is thought to be much slower than HCN formation by photolysis of iron-cyanides at midday (Broderius and Smith 1980). Addition of ultraviolet light to laboratory toxicity tests increases toxicity by three orders of magnitude for both rainbow trout and *Daphnia magna* (Clark *et al.* 1984). Toxicity increases with increasing light intensity (Meyn *et al.* 1984).

The effect of temperature on the toxicity of cyanide is dependent on the concentrations of cyanide used (Wuhrmann and Woker 1955). At relatively low concentrations, cyanide was more toxic at a lower temperature (Smith *et al.* 1978; Kovacs 1979; Kovacs and Leduc 1982). When rapidly lethal concentrations were tested, cyanide was generally more toxic at high temperatures (Cairns and Scheier 1963). Tolerance to cyanide increases with increasing acclimation temperature. The 96-h LC_{50} for juvenile rainbow trout increased significantly with increasing acclimation temperature (Kovacs 1979; Kovacs and Leduc 1982).

The toxicity of cyanide increases with decreases in dissolved oxygen below the saturation level (Doudoroff 1976; Smith *et al.* 1978). The lethal thresholds for several fish species were lowered 20-30% when the oxygen concentration was decreased by 50% (Smith *et al.* 1978). The effect of dissolved oxygen levels is expected to vary with the concentration of cyanide (Leduc *et al.* 1982).

The toxicity of cyanide is influenced by the presence and concentrations of other contaminants in the water. Sublethal concentrations of cyanide in the presence of other contaminants may elicit antagonistic, additive or synergistic responses, depending on the contaminants involved (Speyer 1975; Broderius and Smith 1979). Situations involving multiple toxicity should be considered on a site-specific basis.

The long-term survival and growth of various fish species are seriously reduced at free cyanide concentrations below the mean acute value for exposure of rainbow trout, the most sensitive species tested. Chronic toxicity concentrations for exposure of the bluegill, brook trout and fathead minnow are 13.57, 7.85 and 16.39 $\mu g\cdot L^{-1}$, respectively (Koenst *et al.* 1977; Lind *et al.* 1977; Kimball *et al.* 1978). A relative performance index curve (a single generalized response curve to HCN) suggested a 50% reduction of total performance of cold-water fish continuously exposed to 10 $\mu g\cdot L^{-1}$ free cyanide (as HCN) for 20-30 d under laboratory conditions (Leduc 1977). In the concentration range of 3-5 $\mu g\cdot L^{-1}$, free cyanide would cause relatively minimal impairment of the relative performance index of freshwater fish in water of 10-13°C. Such a range coincides with those proposed by Doudoroff *et al.* (1979), Doudoroff (1980) and the U.S. EPA (1980e, 1985g).

Table 3-6. Guidelines for Dissolved Oxygen

	Dissolved oxygen concentration (mg·L^{-1})	
Categories of biota	Early life stages	Other life stages
Warm-water	6	5
Cold-water	9.5 (6.5)[1]	6.5

[1] Interstitial water of the gravel.

Source: Modified from U.S. EPA 1986.

Table 3-7. Minimum Dissolved Oxygen Concentrations at Different Levels of Fishery Protection

	Dissolved oxygen concentration (mg·L^{-1})			
	Salmonid waters[1]		Nonsalmonid waters	
Level of production impairment	Embryo larva	Other stages	Embryo larva	Other stages
None	11 (8)	8	6.5	6
Slight	9 (6)	6	5.5	5
Moderate	8 (5)	5	5	4
Severe	7 (4)	4	4.5	3.5
Acute mortality	6 (3)	3	4	3

[1] The intergravel dissolved oxygen concentrations are shown in parentheses (a difference of 3 mg·L^{-1} between the water column and the intergravel concentrations has been assumed).

Source: U.S. EPA 1986.

Freshwater plants show a wide range of sensitivities to cyanide. The most sensitive was the green alga (*Scenedesmus quadricauda*); incipient inhibition of this alga occurred at a cyanide concentration of 30 μg·L^{-1} (Bringmann and Kuhn 1977, 1978b). Adverse effects on plants are unlikely at concentrations which are not chronically toxic to fish species.

Biomagnification of cyanide has not been demonstrated (U.S. EPA 1985g).

The numerical limit of 5.0 μg·L^{-1}, proposed by the Ontario Ministry of the Environment (1984) and IJC (1978a), is recommended as a guideline because more recent literature supports this value. The measurement of free cyanide is recommended because it is the primary toxic form and the form measured in toxicity tests; however, sample preservation and analytical problems may make monitoring for free cyanide unreliable, particularly in waters affected by mine wastes. In such cases, the measurement of weak-acid-dissociable cyanide and total cyanide is tentatively recommended. Where metallocyanide complexes, especially iron-cyanide complexes, may be present, the measurement of total cyanide is recommended.

3.2.1.10 Dissolved Oxygen

3.2.1.10.1 Guideline

The concentration of dissolved oxygen should not be less than those concentrations shown in Table 3-6. When applying these guidelines natural variations in dissolved oxygen concentrations must be taken into account.

Table 3-8. Numerical Limits for Ambient Dissolved Oxygen as Proposed by U.S. EPA (1986)

	Ambient dissolved oxygen limits (mg·L^{-1})			
	Cold water		Warm water	
Description	Early life stages	Other life stages	Early life stages	Other life stages
30-d mean	NA[1]	6.5	NA	5.5
7-d mean	9.5 (6.5)	NA	6.0	NA
Minimum	NA	5.0	NA	4.0
1-d minimum	8.0 (5.0)	4.0	5.0	3.0

[1] NA = not applicable.

Source: U.S. EPA 1986.

Until more data are available, the dissolved oxygen concentration in the interstitial water of the gravel should be considered to be at least 3 mg·L^{-1} lower than the oxygen concentration in the overlying water (U.S. EPA 1986). In salmonid spawning habitats, the water column concentration of dissolved oxygen should, therefore, be 9.5 mg·L^{-1}, so that the interstitial concentration (shown in parentheses) is 6.5 mg·L^{-1}. The guideline for the early life stages applies from spawning through to 30 d after hatching. In eutrophic waters, minimum concentrations may occur at night (or dawn) because of diurnal cycling.

3.2.1.10.2 Summary of Documents

The U.S. EPA (1976) recommended a minimum concentration of 5.0 mg·L^{-1} dissolved oxygen to maintain good fish populations. The numerical limit for salmonid spawning beds was a minimum of 5.0 mg·L^{-1} in the interstitial water of the gravel.

The U.S. EPA published new criteria for dissolved oxygen in 1986 (U.S. EPA 1986). This document (U.S. EPA 1986) contains a thorough updating of the literature; it separates cold-water from warm-water species, and it separates early life stages from other stages. The document estimates four levels of impairment for different species and stages (Table 3-7). The proposed numerical limits include mean (7- and 30-d) and minimum (7- and 1-d) values (Table 3-8).

Davis (1975) differentiated between fish populations, temperatures and levels of risk. Dissolved oxygen concentrations were expressed as percent saturation. The limits recommended by Davis (1975), which emphasize the Canadian environment, form the foundation for provincial values for aquatic life prepared since 1975 (Ontario Ministry of the Environment 1979; Williamson 1983). Table 3-9 summarizes the recommended limits for the most common species groups and an intermediate degree of risk. Larvae and eggs of salmonids require higher levels of saturation (76-95%) than those shown for salmonid populations generally.

The IJC stated that in the connecting channels and in the upper lakes of the Great Lakes, the dissolved oxygen concentration should not be less than 6 mg·L^{-1} at any time; in hypolimnetic waters, it should be not less than the concentration necessary for the support of fish life, particularly cold-water species (IJC 1978b). This remained the same as the numerical value in the 1972 agreement (IJC 1972), even though there was some discussion on recommending two levels (IJC 1980).

Because dissolved oxygen levels fluctuate naturally and the available data are limited, the EIFAC Working Party on Water Quality Criteria for European Freshwater Fish tentatively sug-

Table 3-9. Dissolved Oxygen Limits as Recommended by Davis (1975)

Temperature (°C)	Dissolved oxygen limits[1]					
	Warm-water biota		Cold-water biota		Primarily salmonids	
	% Sat.	mg·L^{-1}	% Sat.	mg·L^{-1}	% Sat.	mg·L^{-1}
0	47	7	54	8	57	8
5	47	6	54	7	57	7
10	47	5	54	6	57	6
15	47	5	54	6	59	6
20	47	4	57	5	65	6
25	48	4	63	5	72	6

[1] Expressed as percent saturation.

Source: Davis 1975.

gested that for moderately tolerant freshwater species, the annual 50- and 5-percentile dissolved oxygen concentrations should be greater than 5 and 2 mg·L^{-1}, respectively, and for salmonids the 50- and 5-percentile concentrations should be 9 and 5 mg·L^{-1}, respectively (Alabaster and Lloyd 1982).

The preceding dissolved oxygen limits are minimum values; numerical limits for maximum (supersaturation) levels are not included herein, although supersaturation may cause gas bubble trauma in fish.

3.2.1.10.3 Rationale

The dissolved oxygen requirements of cold-water fish are assumed to be similar to requirements for salmonids, although there are only a few data to support this. Smelts, pikes and sculpins are at least as sensitive. Walleye and smallmouth bass are also moderately sensitive. When no such fish species are present, the warm-water guidelines apply.

Data on the tolerance for low dissolved oxygen concentrations are available for only a few species of nonsalmonid fish. Larval and juvenile nonsalmonids are frequently more sensitive to exposures to low dissolved oxygen than are other life stages (U.S. EPA 1986).

Few appropriate data are available on the effects of low dissolved oxygen on freshwater invertebrates. If, however, all life stages of fish are protected, the invertebrate communities should also be reasonably protected, although they may not be unchanged (Davis 1975).

The combination of low dissolved oxygen and toxic chemicals may lead to stress responses in aquatic organisms. The toxicities of zinc, lead, copper, pentachlorophenol, cyanide, hydrogen sulphide and ammonia are enhanced by low dissolved oxygen.

Higher water temperatures increase the adverse effects of low dissolved oxygen on fish. Because high temperature and low dissolved oxygen commonly occur together in natural environments, the additive or synergistic effect of these two potential stresses is an important consideration. The recommended guidelines are protective at high seasonal environmental temperatures. Maintenance of adequate oxygen at high temperatures is important for fish growth, because fish normally attain high growth rates at high temperatures. Growth under fluctuating oxygen concentrations is almost always less than growth at a constant concentration equal to the mean concentration (U.S. EPA 1986).

The recommended guidelines represent dissolved oxygen concentrations believed to protect the more sensitive populations of organisms against potentially damaging production impairment. The guidelines are derived from a condensation of U.S. EPA information which gives dissolved oxygen in mg·L^{-1} and not as percent saturation, and states that all minima should be considered as instantaneous considerations to be achieved at all times (U.S. EPA 1986).

3.2.1.11 Iron

3.2.1.11.1 Guideline

The concentration of total iron should not exceed 0.3 mg·L^{-1}.

3.2.1.11.2 Summary of Documents

The IJC (1978a) has established a numerical limit for total iron in the Great Lakes of 0.3 mg·L^{-1}, which is the same as the limit set by the Ontario Ministry of the Environment (1984). The Manitoba limit is 1.0 mg·L^{-1} (Williamson 1983), which is the same as the U.S. EPA (1976) recommendation. More recent criteria documents published by the U.S. EPA have not included iron.

3.2.1.11.3 Rationale

The toxicity of iron to invertebrates is variable. Acute toxicity to aquatic insects occurred at iron concentrations ranging from 0.32 to 16.0 mg·L^{-1} (Warnick and Bell 1969). The most sensitive species was the mayfly (*Ephemerella subvaria*), but it was also unusually sensitive to all metals included in the test. The safe concentration for reproduction and growth of *Gammarus minus* was less than 3.0 mg·L^{-1} (Sykora *et al*. 1972). The 3-week LC_{50} for *Daphnia magna* was 5.9 mg·L^{-1} (Biesinger and Christensen 1972).

The fathead minnow appears to be more sensitive to iron than is brook trout. A 50% reduction in the hatchability of fathead minnow eggs occurred at an iron concentration of 1.5 mg·L^{-1} but the hatchability of brook trout eggs was affected at 12.0 mg·L^{-1} (Sykora *et al*. 1972; Smith *et al*. 1973). The safe concentration for exposure of brook trout (*Salvelinus fontinalis*), based on the mortality of juveniles, was between 7.5 and 12.52 mg·L^{-1}. The iron hydroxide precipitate interferes with respiration through the chorion in fish eggs, and impairs gill function by occlusion of the lamellae (Sykora *et al*. 1972).

Because the numerical limit established by the Province of Ontario and the IJC appears to provide adequate protection to fish (based on the limited chronic data available) and to most invertebrates, it is recommended until further data are available. A concentration of 1.0 mg·L^{-1} appears to be too close to the EC_{50} for the fathead minnow to offer adequate protection.

3.2.1.12 Lead

3.2.1.12.1 Guideline

The concentration of total lead should not exceed the concentrations shown in Table 3-10.

Table 3-10. Recommended Guidelines for Total Lead for Waters of Different Hardness

Hardness (mg·L^{-1} as $CaCO_3$)		Concentration of lead (µg·L^{-1})
0-60	(soft)	1
60-120	(medium)	2
120-180	(hard)	4
>180	(very hard)	7

3.2.1.12.2 Summary of Documents

The U.S. EPA (1976) proposed a numerical limit for lead which was 0.01 times the 96-h LC_{50} value, using soluble lead measurements and the receiving or comparable water as the diluent, for sensitive freshwater resident species. This was replaced by the U.S. EPA (1980f) with a 24-h and an instantaneous limit based on formulae pertaining to water hardness. At hardnesses of 50, 100 and 200 mg·L^{-1} as $CaCO_3$, the 24-h average concentrations were 0.75, 3.8 and 20 µg·L^{-1}, respectively, and the instantaneous maxima were 74, 170 and 400 µg·L^{-1}, respectively. The U.S. EPA (1985h) replaced the 1980 numerical limits with new values that allow an excess concentration every 3 years on the average. The hardness formulae and the averaging periods were also revised. At hardnesses of 50, 100 and 200 mg·L^{-1} as $CaCO_3$, the 4-d average concentrations of lead were 1.3, 3.2 and 7.7 µg·L^{-1}, respectively, and the 1-h average concentrations were 34, 82 and 200 µg·L^{-1}, respectively (U.S. EPA 1985h). The U.S. EPA (1985h) recommended measurement of acid-soluble lead; however, the measurement of total recoverable lead has been recommended until an acid-soluble method is approved.

Demayo *et al.* (1980) recommended lead concentrations of 0.005 and 0.01 mg·L^{-1} (total lead) at hardnesses of less than 95 mg·L^{-1} (as $CaCO_3$) and greater than 95 mg·L^{-1}, respectively. A limit of 0.03 mg·L^{-1} was recommended for waters where sensitive species of fish are absent. The IJC (1980) recommended 2.0, 3.0, 4.0 and 5.0 µg·L^{-1} (total lead) for Lake Superior, Lake Huron, Lake Michigan and Lake Ontario, respectively. A note of caution was given that the recommendation would not necessarily protect aquatic biota from the effects of alkyllead compounds. Ontario's (Ontario Ministry of the Environment 1984) numerical limits are 5.0, 10.0, 20.0 and 25.0 µg·L^{-1} (total lead) at alkalinities of less than 20, 20-40, 40-80 and greater than 80 mg·L^{-1} as $CaCO_3$, respectively. Manitoba (Williamson 1983) has established limits of 0.75, 3.8 and 20.0 µg·L^{-1} at hardnesses of 50, 100 and 200 mg·L^{-1} as $CaCO_3$, respectively.

3.2.1.12.3 Rationale

The acute toxicity of lead is greater in soft water than in hard water. The effect of hardness on toxicity has been demonstrated for rainbow trout (*Salmo gairdneri*), fathead minnows (*Pimephales promelas*), bluegill (*Lepomis macrochirus*) and *Daphnia magna* (U.S. EPA 1985h). The effect of hardness on the last three species is very similar, whereas the effect on rainbow trout is quite different.

In acute toxicity tests, amphipods are apparently more sensitive to lead than are any other freshwater animal species included in standard tests. The species mean acute toxicity concentrations for exposure of the four most sensitive species tested, the amphipod *Gammarus pseudolimnaeus*, the cladoceran *Daphnia magna*, rainbow trout and brook trout (*Salvelinus fontinalis*), were 142.6, 447.8, 2448 and 4820 µg·L^{-1}, respectively (U.S. EPA 1985h).

The chronic toxicity of lead also decreases with increasing water hardness. Daphnids are nearly 11 times more sensitive to lead in soft water than in hard water. Reproduction of *Daphnia magna* was impaired 16% by 0.03 mg·L^{-1} in soft water. In soft water, 44% of the trout developed spinal deformities at measured lead concentrations of 31 µg·L^{-1}; in hard water, however, none of the rainbow trout developed deformities at concentrations of 190 µg·L^{-1} (Biesinger and Christensen 1972).

In a life-cycle test with a snail (*Lymnaea palustris*) (Borgmann *et al.* 1978), no effect on survival was observed at a lead concentration of 12 µg·L^{-1}, but almost complete mortality occurred at 54 µg·L^{-1}, giving a chronic toxicity concentration of 25.46 µg·L^{-1} in hard water (139 mg·L^{-1} as $CaCO_3$) (U.S. EPA 1985h). The U.S. EPA (1985h) also calculated chronic toxicity concentrations of 12.26 and 18.88 µg·L^{-1} for exposure of *Daphnia magna* and rainbow trout.

Rainbow trout exposed to lead as fingerlings develop blackening of the tails and spinal curvature. The maximum acceptable toxicant concentration (MATC) for rainbow trout was 4.1-7.6 µg·L^{-1} for fry in soft water (Davies *et al.* 1976); lead affects enzymes at a concentration of 13.0 µg·L^{-1} free lead and a hardness of 135 mg·L^{-1} (Hodson 1976). Brook trout and bluegill have been shown to be less sensitive than rainbow trout. The MATC for brook trout was 39.0 and 84.0 µg·L^{-1} as dissolved lead (58.0 and 119.0 µg·L^{-1} total lead) in soft water (44 mg·L^{-1} as $CaCO_3$) (Holcombe *et al.* 1976). The MATC was very similar to that for the bluegill, which was between 0.07 and 0.12 mg·L^{-1} as total lead, also in soft water (Sauter *et al.* 1976).

The toxicity of lead to algae is relatively low. Adverse effects on algae occur at concentrations ranging from 0.5 to 63.8 mg·L^{-1} (U.S. EPA 1985h).

Rooted macrophytes accumulate lead to a greater degree than do plants without roots (Wong *et al.* 1976). The bioconcentration factors for lead in *Cladophora glomerata* from Lake Ontario ranged from 16 000 to 20 000 (Keeney *et al.* 1976). Lead has not been shown to biomagnify in the aquatic environment (Namminga *et al.* 1974; Getz *et al.* 1977). Bioconcentration factors for four species of invertebrates and two species of fish ranged from 499 to 1700 (U.S. EPA 1985h). Bioconcentration factors obtained with brook trout and bluegills were 42 and 45, respectively (Holcombe *et al.* 1976; Atchison *et al.* 1977).

The U.S. EPA (1985h) hardness formula for chronic toxicity (4-d average lead concentration) is used to derive the guideline:

$$\text{Pb conc.} = e^{(1.273[\ln(\text{hardness})] - 4.705)}\ \mu\text{g}\cdot\text{L}^{-1}$$

The guideline for soft water was calculated using a hardness of 50 mg·L^{-1} as $CaCO_3$, because toxicity data for very soft waters are not available. There is the possibility of under protection in very soft water.

3.2.1.13 Mercury

3.2.1.13.1 Guideline

The concentration of total mercury should not exceed 0.1 $\mu g \cdot L^{-1}$.

3.2.1.13.2 Summary of Documents

Reeder *et al.* (1979b) recommended guidelines of 0.1 $\mu g \cdot L^{-1}$ as total mercury to protect the consumers of fish, and 0.2 $\mu g \cdot L^{-1}$ as total mercury to protect aquatic life where fish are not eaten. The numerical limits established by the Ontario Ministry of the Environment (1984) and by the IJC (1976) for the Great Lakes are 0.2 $\mu g \cdot L^{-1}$ and 0.5 $\mu g.g^{-1}$ of total mercury in whole fish as wet weight. The Province of Manitoba (Williamson 1983) established a limit of 0.57 $ng \cdot L^{-1}$, which is similar to the U.S. EPA (1980g) value, except that it is an instantaneous maximum. The effects of mercury in the Canadian environment have been summarized by the NRCC (1979b); however, no numerical limits were recommended.

The U.S. EPA (1976) numerical limit of 0.05 $\mu g \cdot L^{-1}$ was replaced by the U.S. EPA (1980g) values of 0.57 $ng \cdot L^{-1}$ as a 24-h average, and of 1.7 $ng \cdot L^{-1}$ at any time. These limits have recently been superseded (U.S. EPA 1985i). The new values are 0.012 $\mu g \cdot L^{-1}$ as a 4-d average and 2.4 $\mu g \cdot L^{-1}$ as a 1-h average. The limits should not be exceeded more than once every 3 years on the average (U.S. EPA 1985i). The 1985 U.S. EPA values are based on the acid-soluble method, but the U.S. EPA recommends the use of the total recoverable method until an acid-soluble method has been approved.

3.2.1.13.3 Rationale

The range of sensitivities among different species to a single mercury compound is greater than the range of sensitivities of the same species to different compounds (U.S. EPA 1985i).

The U.S. EPA (1985i) summarized data on the toxicity of mercury(II) for 28 genera of freshwater biota. Concentrations acutely toxic to invertebrate species ranged from 2.2 $\mu g \cdot L^{-1}$ for *Daphnia pulex* (Canton and Adema 1978) to 2.0 $mg \cdot L^{-1}$ for a mayfly (*Ephemerella subvaria*) (Warnick and Bell 1969). Concentrations causing acute toxicity to fish ranged from 30 $\mu g \cdot L^{-1}$ for the guppy (*Poecilia reticulata*) (Deshmukh and Marathe 1980) to 1.0 $mg \cdot L^{-1}$ for the tilapia (*Tilapia mossambica*) (Qureshi and Saksena 1980). The most sensitive salmonid species was the juvenile coho salmon (*Oncorhynchus kisutch*), with a species mean acute toxicity concentration of 240 $\mu g \cdot L^{-1}$ (Lorz *et al.* 1978); the fathead minnow (*Pimephales promelas*) and the bluegill (*Lepomis macrochirus*) were more sensitive, with species mean acute toxicity concentrations of 158.7 and 160 $\mu g \cdot L^{-1}$, respectively (Snarski and Olson 1982; Call *et al.* 1983; Holcombe *et al.* 1983). The acute toxicity of mercury to fish appears to increase as temperature increases (Clemens and Sneed 1958; MacLeod and Pessah 1973).

Few data are available for organomercury compounds, but they appear to be more acutely toxic than mercury(II). The lowest LC_{50} for rainbow trout (*Salmo gairdneri*) was 24 $\mu g \cdot L^{-1}$ of methylmercury (Wobeser 1973; Lock and Van Overbeeke 1981; Lock *et al.* 1981).

Methylmercury appears to be the most chronically toxic of the tested mercury compounds; tests with *Daphnia magna* and brook trout (*Salvelinus fontinalis*) resulted in chronic toxicities occurring at less than 0.04 and 0.52 $\mu g \cdot L^{-1}$, respectively (McKim *et al.* 1976; Biesinger *et al.* 1982). The lowest chronic toxicity concentration for mercury(II) was 0.96 $\mu g \cdot L^{-1}$ for exposure of *Daphnia magna*. In life-cycle and early-life-stage tests of mercury(II), the chronic toxicity concentrations for exposure of the fathead minnow were less than 0.26 and less than 0.23 $\mu g \cdot L^{-1}$, respectively (Snarski and Olson 1982; Call *et al.* 1983).

The most sensitive plant species generally appear to be less sensitive than sensitive animal species to both mercury(II) and methylmercury, although the growth of *Chlamydomonas* sp. is severely retarded at a methylmercury concentration of 0.02 $\mu g \cdot L^{-1}$ (Lock 1975).

The accumulation of mercury by organisms is variable. Bottom feeders generally contain more mercury than do animals feeding in the water column (Hamilton 1972; Holm and Cox 1974). Bioconcentration factors are larger for methylmercury than for mercury(II). Bioconcentration factors of 1800 for rainbow trout and 4994 for the fathead minnow have been determined for mercury(II) (Snarski and Olson 1982; Boudou and Ribeyre 1984). Bioconcentration factors for methylmercury in rainbow trout, brook trout and fathead minnows range from 10 000 to 85 700 (Olson *et al.* 1975; McKim *et al.* 1976; Boudou and Ribeyre 1984; Niimi and Lowe-Jinde 1984).

A guideline of 0.1 $\mu g \cdot L^{-1}$ to protect consumers of fish was recommended by Reeder *et al.* (1979b). Recent data support this guideline. Using the maximum bioconcentration factor for mercury(II), 4994 for the fathead minnow (Snarski and Olson 1982), and a maximum permissible mercury concentration in fish flesh of 0.5 $\mu g.g^{-1}$, the concentration in water that should protect the marketability of freshwater fish would be 0.1 $\mu g \cdot L^{-1}$. In addition, the chronic toxicity concentration of mercury(II) for exposure of the fathead minnow, the most sensitive species, is less than 0.23 $\mu g \cdot L^{-1}$ (Call *et al.* 1983). Thus, toxicity and bioaccumulation data both support a guideline of 0.1 $\mu g \cdot L^{-1}$ (total mercury).

Because the bioconcentration factors, chronic toxicities and acute:chronic ratios are greater for methylmercury, the U.S. EPA (1985i) numerical limits derived from tests using methylmercury are approximately an order of magnitude lower than the guideline based on mercury(II). The Canadian approach, which assumes that methylmercury represents a small percentage of total mercury in water (Reeder *et al.* 1979b), has been adopted.

3.2.1.14 Nickel

3.2.1.14.1 Guideline

The concentration of total nickel should not exceed those shown in Table 3-11.

Table 3-11. Recommended Guidelines for Total Nickel for Waters of Different Hardness

Hardness ($mg \cdot L^{-1}$ as $CaCO_3$)		Concentration of nickel ($\mu g \cdot L^{-1}$)
0-60	(soft)	25
60-120	(medium)	65
120-180	(hard)	110
>180	(very hard)	150

3.2.1.14.2 Summary of Documents

The U.S. EPA (1976) proposed a numerical limit for nickel which was 0.01 of the 96-h LC_{50}. Values for total recoverable nickel have recently been based on hardness-related formulae (U.S. EPA 1980h). At water hardnesses of 50, 100 and 200 $mg \cdot L^{-1}$ as $CaCO_3$, the numerical limits are 56, 96 and 160 $\mu g \cdot L^{-1}$, respectively, as 24-h averages, and 1.10, 1.80 and 3.10 $mg \cdot L^{-1}$, respectively, at any time.

Ontario (Ontario Ministry of the Environment 1984) and the IJC (1978a) have recommended 25 $\mu g \cdot L^{-1}$. Taylor, Demayo and Reeder (1979) recommended 25 $\mu g \cdot L^{-1}$ in soft water and 0.25 $mg \cdot L^{-1}$ in water of hardness greater than 150 $mg \cdot L^{-1}$ as $CaCO_3$. The Manitoba numerical limit is the same as the U.S. EPA (1980h) value (total recoverable nickel) for a 24-h average, but it applies to an instantaneous sample. The NRCC (1981) has prepared a document on the effects of nickel in the Canadian environment, although no numerical limits were recommended.

3.2.1.14.3 Rationale

The U.S. EPA (1980h) compiled data on the acute toxicity of nickel to 22 species of aquatic animals. For invertebrates, concentrations causing acute toxicity ranged from a low of 510 $\mu g \cdot L^{-1}$ for *Daphnia magna* (Biesinger and Christensen 1972) to a high of 33.5 $mg \cdot L^{-1}$ for a stonefly (*Acroneuria lycorias*) (Warnick and Bell 1969) (at water hardnesses of less than 50 $mg \cdot L^{-1}$ as $CaCO_3$). Concentrations causing acute toxicity to fish ranged upwards from 2.48 $mg \cdot L^{-1}$ for the rock-bass (*Ambloplites rupestris*) (U.S. EPA 1980h). The only acute toxicity concentration found for a salmonid (*Salmo gairdneri*) was 35.5 $mg \cdot L^{-1}$ at an unknown hardness (Hale 1977).

Nickel is more toxic at lower water hardness. The U.S. EPA (1980h) was able to define a relationship between water hardness and the acute toxicity of three species, *Daphnia magna*, *Daphnia pulicaria* and the fathead minnow (*Pimephales promelas*). Toxicity appears to be increased by increasing acidity. For example, the toxicity of nickel to the alga *Selenastrum capricornutum* decreases markedly as the pH increases above 4 (Michnowicz and Weaks 1984). Nickel is removed from solution by the presence of suspended solids (Taylor, Demayo and Reeder 1979). Toxicity is increased with the addition of copper (Anderson and Weber 1976; Stokes *et al.* 1980). When copper is known to be present, the possibility of synergism must be taken into account (Taylor, Demayo and Reeder 1979).

Mortality occurs at much lower nickel concentrations in early-life-stage tests than in 96-h acute tests with juvenile fish. In an early-life-stage test starting with newly fertilized eggs, the highest concentration of nickel which did not cause significant effects in rainbow trout was 35 $\mu g \cdot L^{-1}$ at a hardness of less than 50 $mg \cdot L^{-1}$ (Nebeker *et al.* 1985). This concentration was similar to the nickel avoidance threshold value of 23.9 $\mu g \cdot L^{-1}$ found by Giattina *et al.* (1982) for rainbow trout. When the early-life-stage tests were started with eyed eggs or pre-swim-up larvae, the results, 134 $\mu g \cdot L^{-1}$ in both cases, were similar to the results for the fathead minnow. In water of similar softness, the result of an early-life-stage test with the fathead minnow was a concentration of 109 $\mu g \cdot L^{-1}$ (U.S. EPA 1980h). The maximum acceptable toxicant concentration was between 0.73 and 0.38 $mg \cdot L^{-1}$ for fathead minnows (Pickering 1974). Chronic values ranged from 14.8 $\mu g \cdot L^{-1}$ for *Daphnia magna* in soft water to 530 $\mu g \cdot L^{-1}$ for the fathead minnow in hard water (U.S. EPA 1980h). Reduced growth of several freshwater algal species occurred at concentrations ranging from 100 to 700 $\mu g \cdot L^{-1}$, but the water hardness was unknown (Hutchinson 1973; Hutchinson and Stokes 1975).

Biomagnification is not significant in the aquatic environment (Taylor, Demayo and Reeder 1979). Nickel decreased in concentration at increasing levels of the food web. Equilibrium concentrations of nickel were highest in plants, intermediate in invertebrates and lowest in the top predators (Hutchinson *et al.* 1975). Annelida contain more nickel than do other members of the food web; carnivorous fish contain less than omnivorous fish (Mathis and Cummings 1973). The available bioconcentration factors are 9.8, 100 and 61 for nickel exposure of an alga, *Daphnia magna* and the fathead minnow, respectively (U.S. EPA 1980h). More recently, Watras *et al.* (1985) found that the alga *Scenedesmus obliquus* concentrated nickel to concentrations 30-300 times above ambient concentrations, whereas the invertebrate *Daphnia magna* concentrated nickel to levels only slightly above ambient concentrations.

Taylor, Demayo and Reeder (1979) reconfirmed the numerical limit of 25 $\mu g \cdot L^{-1}$ established earlier by the IJC (1976) and the Ontario Ministry of the Environment (1984). More recent data show only one chronic response for the invertebrate *Daphnia magna* below this concentration; therefore, adoption of the above guideline is recommended for soft water. Taylor, Demayo and Reeder (1979) recognized that a less stringent guideline for hard waters could be used. The hardness-related formula of the U.S. EPA (1980h) is used to calculate the guidelines for medium to hard waters:

$$\text{Ni conc.} = e^{(0.76[\ln(\text{hardness})] + 1.06)} \ \mu g \cdot L^{-1}$$

Replacing the guideline recommended by Taylor, Demayo and Reeder (1979) for hard waters (>150 $mg \cdot L^{-1}$ as $CaCO_3$) with the U.S. EPA (1980h) formula allows for the calculation of site-specific water quality objectives where the water hardness is known (if so desired). Guidelines using four hardness categories are recommended and appear in Table 3-11.

3.2.1.15 Nitrogen (Ammonia, Nitrates, Nitrites, Nitrosamines)

3.2.1.15.1 Guideline

The concentration of total ammonia should not exceed those shown in Table 3-12. Although un-ionized ammonia is

Table 3-12. Recommended Guidelines for Total Ammonia (NH_3)

	Ammonia concentration ($mg \cdot L^{-1}$) at following temperatures (°C)						
pH	0	5	10	15	20	25	30
6.50	2.5	2.4	2.2	2.2	1.49	1.04	0.73
6.75	2.5	2.4	2.2	2.2	1.49	1.04	0.73
7.00	2.5	2.4	2.2	2.2	1.49	1.04	0.74
7.25	2.5	2.4	2.2	2.2	1.50	1.04	0.74
7.50	2.5	2.4	2.2	2.2	1.50	1.05	0.74
7.75	2.3	2.2	2.1	2.0	1.40	0.99	0.71
8.00	1.53	1.44	1.37	1.33	0.93	0.66	0.47
8.25	0.87	0.82	0.78	0.76	0.54	0.39	0.28
8.50	0.49	0.47	0.45	0.44	0.32	0.23	0.17
8.75	0.28	0.27	0.26	0.27	0.19	0.16	0.11
9.00	0.16	0.16	0.16	0.16	0.13	0.10	0.08

Source: U.S. EPA 1985j.

the toxic component, note that the table shows the equivalent concentration of total ammonia for each combination of temperature and pH. Thus, calculation of un-ionized ammonia is unnecessary. The toxicity of un-ionized ammonia varies with pH and temperature, and the portion of total ammonia that is un-ionized also varies with pH and temperature. The total ammonia guidelines recommended in Table 3-12 reflect both of these variations.

The concentration of nitrite should not exceed 0.06 $mg \cdot L^{-1}$. A numerical guideline is not recommended for nitrate, but excessive amounts of nitrate should be avoided because it may cause prolific weed growth.

There are insufficient data to recommend a guideline for nitrosamines.

3.2.1.15.2 Summary of Documents

The Province of Manitoba (Williamson 1983) recommended that nitrogen (total organic and inorganic) should be limited to prevent the nuisance growth of aquatic rooted, attached and floating plants, fungi, etc. which would render the water unsuitable for other beneficial uses. The Alberta (Alberta Ministry of the Environment 1977) and Saskatchewan (Saskatchewan Ministry of the Environment 1983) multipurpose water quality objectives for total organic and inorganic nitrogen are 1 $mg \cdot L^{-1}$. No other published guidelines pertaining to the protection of aquatic life were found for total nitrogen, nitrates or nitrites, though British Columbia is in the process of developing them.

The provinces of Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) established a limit of 0.02 $mg \cdot L^{-1}$ of un-ionized ammonia to protect aquatic life. This limit is the same as the U.S. EPA (1976) value. The IJC recently revised its numerical limit from 0.02 $mg \cdot L^{-1}$ un-ionized ammonia to 0.03 $mg \cdot L^{-1}$ for all waters except special use zones; the requirement for the latter is expressed by an equation (IJC 1986). The U.S. EPA (1985j) revised its limits to include formulae for 1-h and 4-d average concentrations for waters where salmonids or other sensitive cold-water species are either present or absent. The U.S. EPA (1985j) recently permitted concentrations to exceed numerical limits by an unspecified amount once every 3 years on average.

The U.S. EPA (1980i) prepared a document on the ambient water quality criteria for nitrosamines, but limits were not established because the U.S. EPA's minimum data base requirements were not met. No other guidelines pertaining to nitrosamines were found, although the Ontario Ministry of the Environment (1984) listed nitrosamines as substances with undefined tolerance limits.

3.2.1.15.3 Rationale

Nitrate is a major nutrient for aquatic vegetation. Because nitrates may stimulate plant growth, excessive amounts of nitrate may result in prolific growth. In acute toxicity tests with nitrate-nitrogen, the 96-h LC_{50} values for chinook salmon (*Oncorhynchus tshawytscha*) and fingerling rainbow trout (*Salmo gairdneri*) were 5.80 and 6.00 $g \cdot L^{-1}$, respectively (Westin 1974). Steelhead and rainbow trout eggs and chinook salmon fry showed a significant increase in mortality at nitrate exposures as low as 5, 10 and 20 $mg \cdot L^{-1}$, respectively (Kincheloe *et al.* 1979).

Salmonids are more sensitive to nitrite than are other fish species and show very little difference among the species (Lewis and Morris 1986). In acute toxicity tests with nitrite-nitrogen, the 96-h LC_{50} for chinook salmon (*Oncorhynchus tshawytscha*) was 2.9 $mg \cdot L^{-1}$ (Westin 1974). In flow-through nitrite bioassays, the 96-h LC_{50} levels for four sizes of rainbow trout (*Salmo gairdneri*) ranged from 0.19 to 0.39 $mg \cdot L^{-1}$ (Russo *et al.* 1974). There is considerably more variation among warm-water fish species (Lewis and Morris 1986). The 96-h LC_{50} values of nitrite-nitrogen for channel catfish (*Ictalurus punctatus*), tilapia (*Tilapia aurea*) and largemouth bass (*Micropterus salmoides*) were 7, 16 and 140 $mg \cdot L^{-1}$, respectively (Palachek and Tomasso 1984).

Lewis and Morris (1986) concluded, from the available literature, that small fish (including the larval stage) are unlikely to be more sensitive to nitrite than larger fish of the same species. They found some evidence that for some species, small fish are more tolerant to nitrite toxicity than fish of intermediate or large size.

The concentration of nitrite at which no rainbow trout died over 10 d was 0.06 $mg \cdot L^{-1}$ (Russo *et al.* 1974). Steelhead juveniles exposed for 6 months showed increased methemoglobin levels at 0.015 $mg \cdot L^{-1}$, but tissue damage was not noted in the gills until the concentration was 0.06 $mg \cdot L^{-1}$ (Wedemeyer and Yasutake 1978). No reduction in growth occurred over 6 months' exposure to 0.06 $mg \cdot L^{-1}$ at chloride concentrations of 2.3 $mg \cdot L^{-1}$. Addition of chloride ions can increase the tolerance of salmonid fish to nitrite (Wedemeyer and Yasutake 1978).

Methemoglobin, a derivative of hemoglobin which is incapable of binding with oxygen, has been observed in fish and amphibians (Smith and Williams 1974; Russo *et al.* 1974; Huey *et al.* 1980; Huey and Beitinger 1980). Nevertheless, liver hypoxia is thought to be the cause of nitrite toxicity (Arillo *et al.* 1984).

Concentrations of nitrate- and nitrite-nitrogen of 90 and 5 $mg \cdot L^{-1}$, respectively, would be protective of most warm-water fish (McCoy 1972; Knepp and Arkin 1973). Nitrite concentrations at or below 0.06 $mg \cdot L^{-1}$ should protect salmonid fish (Russo *et al.* 1974; Russo and Thurston 1975). Because these levels either are not known to occur or would be unlikely to occur in natural surface waters, the U.S. EPA (1976) did not set numerical limits.

The U.S. EPA (1985j) found that ammonia was acutely toxic to freshwater organisms at concentrations (uncorrected for pH) ranging from 0.53 to 22.8 mg·L^{-1} for 19 invertebrate species representing 14 families, and from 0.083 to 4.60 mg·L^{-1} for 29 fish species from 9 families. The 96-h LC$_{50}$s ranged upwards from 0.083 mg·L^{-1} for salmonids and from 0.143 mg·L^{-1} for nonsalmonids (Rice and Bailey 1980; Thurston and Meyn 1984). There was, however, considerable overlap between salmonids and nonsalmonids; the five most sensitive species were, in order of sensitivity, mountain whitefish (*Prosopium williamsoni*), golden shiner (*Notemigonus crysoleucas*), orangethroat darter (*Etheostoma spectabile*), walleye (*Stizostedion vitreum*) and rainbow trout (Hazel *et al.* 1979; Swigert and Spacie 1983; Thurston and Russo 1983; Thurston and Meyn 1984; West 1985). The acute toxicity of ammonia to rainbow trout has been studied by many investigators using flow-through tests and measured concentrations; the 96-h LC$_{50}$s ranged from 0.16 to 1.1 mg·L^{-1} (Calamari *et al.* 1977, 1981; Broderius and Smith 1979; DeGraeve *et al.* 1980; Thurston, Phillips *et al.* 1981; Thurston, Russo *et al.* 1981; Reinbold and Pescitelli 1982; Thurston and Russo 1983; West 1985). Chronic toxicity occurred at concentrations which ranged upwards from 1.7 μg·L^{-1} for pink salmon (*Oncorhynchus gorbuscha*) (Rice and Bailey 1980).

Un-ionized ammonia (NH$_3$) has been demonstrated to be the principal toxic form of ammonia. Modifying factors may alter the acute toxicity by altering the concentration of un-ionized ammonia in the water through changes in the ammonia-ammonium ion equilibrium, or by increasing the toxicity of the un-ionized ammonia to the organisms. Factors that have been shown to affect ammonia toxicity include dissolved oxygen concentration, carbon dioxide concentration, salinity, temperature, pH, previous acclimation to ammonia, fluctuations in exposure and the presence of other toxicants (U.S. EPA 1985j). The effect of total dissolved solids has been shown to be minor in fresh water (Messer *et al.* 1984) and is not considered in proposing guidelines. More information is available for temperature and pH effects. The acute toxicity of ammonia to fish increases as dissolved oxygen, pH and temperature decrease. Fish with a history of prior exposure to sublethal concentrations of ammonia are better able to withstand concentrations that would otherwise be acutely lethal. Fish are more tolerant of constant concentrations of ammonia than of fluctuating concentrations.

Invertebrates are generally more tolerant than fish, with the exception of the fingernail clam (*Musculium transversum*) (Anderson *et al.* 1978). Phytoplankton and aquatic vascular plants are appreciably more tolerant to ammonia than are invertebrates or fish (Abelovich and Azov 1976; Przytocka-Jusiak 1976).

The numerical limit proposed by the U.S. EPA (1985j) for total ammonia for sensitive cold-water species (on a 4-d average) has been adopted as a Canadian guideline because the U.S. EPA values are derived from the largest and most recent data base. Sufficient data exist from toxicity tests conducted at different pH and temperature values to describe temperature- and pH-dependent acute ammonia toxicity. The very limited number of data on chronic toxicity also indicates increasing ammonia toxicity with decreasing pH. There is no information available regarding temperature effects on chronic ammonia toxicity, although sufficient data exist to demonstrate the effect of temperature on acute toxicity. In spite of their limitations, the average numerical limits of the U.S. EPA (1985j) have been recommended over the recent IJC (1986) limit of 0.03 mg·L^{-1} un-ionized ammonia because aquatic life in water bodies with an average pH below 7.8 may not be protected by a single number guideline, particularly under cold temperatures.

The U.S. EPA (1985j) limits include two different classifications of waters; the Canadian guidelines do not. The U.S. EPA (1985j) criteria document states that there is no clear trend among groups of fish; the most sensitive species and genera tested include representatives from diverse families.

In static tests for the acute toxicity of the nitrosamine N-nitrosodiphenylamine, the EC$_{50}$ concentrations for the bluegill and the cladoceran, *Daphnia magna*, were 5.85 and 7.76 mg·L^{-1}, respectively. The bioconcentration factor for the same compound was 217 in the bluegill, but the tissue half-life was less than 1 d (U.S. EPA 1980i).

Standard toxicity data on the chronic toxicity of nitrosamines are not available; however, chronic feeding studies with rainbow trout and N-nitrosodimethylamine showed a dose-related response of hepatocellular carcinoma over a feeding range of 200-800 mg·kg^{-1} (Grieco *et al.* 1978).

3.2.1.16 pH

3.2.1.16.1 Guideline

For the protection of aquatic life, the pH of water should not vary beyond the range of pH 6.5-9.0.

3.2.1.16.2 Summary of Documents

The Manitoba objective (Williamson 1983) and the IJC (1975) recommended a pH range of 6.5-9.0 to protect aquatic life. The IJC objective also states that discharges should not change the pH at the boundary of the designated mixing zone more than 0.5 units from the ambient. The U.S. EPA (1976) established the same range of 6.5-9.0. Ontario (Ontario Ministry of the Environment 1984) has recommended a range of pH 6.5-8.5. EIFAC (Alabaster and Lloyd 1982) did not set a single range for the protection of European fisheries; its recommendation is summarized in a table of ranges (Table 3-13).

3.2.1.16.3 Rationale

Data on pH have been summarized by Hendrey *et al.* (1976), Leivestad *et al.* (1976), Fromm (1980) and Alabaster and Lloyd (1982). There is no definite pH range within which a fishery is unharmed and outside of which it is damaged, but rather there is a gradual deterioration of water quality as pH values are removed from the normal range (EIFAC 1969). The pH range which is not acutely lethal to fish is pH 5-9. Individual fish species have an optimum pH within this range (Alabaster and Lloyd 1982); however, the toxicity of several common pollutants is markedly affected by pH changes within this range, and increasing acidity or alkalinity may make these pollutants more toxic. Also, an acid discharge may liberate sufficient carbon dioxide from bicarbonate to cause the pH range of 5-6

Table 3-13. Summary of the Effects of pH Values on Fish

pH range	Effect
3.0-3.5	Unlikely that any fish can survive for more than a few hours in this range, although some plants and invertebrates can be found at pH values lower than this.
3.5-4.0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, nonlethal levels, but the lower end of this range may still be lethal for roach.
4.0-4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4.5-5.0	Likely to be harmful to the eggs and fry of salmonids, and to adults particularly in soft water containing low concentrations of calcium, sodium and chloride. Can be harmful to common carp.
5.0-6.0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 mg·L^{-1}, or the water contains iron salts which are freshly precipitated as ferric hydroxide, the precise toxicity of which is not known. The lower end of this range may be harmful to nonacclimated salmonids if the calcium, sodium and chloride concentrations or the temperature of the water are low, and may be detrimental to roach production.
6.0-6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 mg·L^{-1}.
6.5-9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0-9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5-10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to developmental stages of some species.
10.0-10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5-11.0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11.0-11.5	Rapidly lethal to all species of fish.

Source: Alabaster and Lloyd 1982.

to become lethal. At lower concentrations of calcium, the toxicity of elevated hydrogen ion concentrations to fish is increased (McDonald 1983).

Chronic effects have been reported within the pH range of 5-6. Loss of fish populations has been attributed to spawning failure and diminished hatching success at moderately acidic pH levels (<pH 6.0) (Schofield 1976; Harvey 1979; Fromm 1980). Exposure to acid-treated water (pH 4.2-6.0) for 21 d altered the head kidney (interrenal) and thyroid function in immature rainbow trout (*Salmo gairdneri*) (Brown *et al*. 1984). In rainbow trout exposed for 22 d to water at pH 4.2-6.0, hematocrit and hemoglobin concentrations increased progressively with acid stress below pH 5.5 (Giles *et al*. 1984). Most of the histological effects of chronic acid stress on fathead minnows were seen at pH 5.5 and 5.0, and were confined to changes in numbers, distribution and morphology of chloride cells (Leino and McCormick 1984).

The most commonly accepted lower limit for pH is 6.5 rather than 6. This limit is substantiated by bioassays showing that egg production and hatchability of the fathead minnow (Mount 1973) and emergence of aquatic insects (Bell 1971) were decreased at pH values below 6.6. Bluegill and brook trout demonstrated increased ventilatory responses at pH levels of 6.7 and 6.0, respectively (Carlson 1984).

The most common upper limit for pH is 9; pH values between 9 and 10 may be harmful to a few species of fish (Alabaster and Lloyd 1982). Bluegill showed an increase in coughing above pH 9, but brook trout were not affected up to pH 10.1 (Carlson 1984). When rainbow trout were exposed to an increase of pH to 9.5 in 6 h, 50% mortality occurred; at an increase of pH to 9.3 in 6 h, a temporary loss of appetite was the only change observed (Murray and Ziebell 1984).

3.2.1.17 Selenium

3.2.1.17.1 Guideline

The concentration of total selenium should not exceed 1 μg·L^{-1}.

3.2.1.17.2 Summary of Documents

The IJC recommended 1 μg·L^{-1} in unfiltered water; 5 μg.g^{-1} in sediments; and 3 μg.g^{-1} (wet weight) in aquatic biota to protect predatory fish and mammals (IJC 1981). Demayo *et al*. (1979b) recommended a guideline of 0.01 mg·L^{-1}. Ontario recommended a numerical limit of 0.1 mg·L^{-1} (Ontario Ministry of the Environment 1984).

The U.S. EPA (1980j) established a numerical limit for selenium of 35 μg·L^{-1} as a 24-h average and 260 μg·L^{-1} at any time. It replaced an earlier value which was 0.01 of the 96-h LC$_{50}$ as determined through bioassay using a sensitive resident species (U.S. EPA 1976). The Manitoba numerical limit, 35 μg·L^{-1} (total selenite), is numerically the same as the U.S. EPA value for a 24-h average, but is an instantaneous maximum concentration not to be exceeded at any time (Williamson 1983).

3.2.1.17.3 Rationale

There does not appear to be a great difference in the toxicities of selenite and selenate, although selenite may be slightly more toxic than selenate. Selenium, however, is known to be methylated biologically in lake sediments (Chau *et al*. 1976); selenomethionine is 10 times more toxic than the inorganic form (Niimi and LaHam 1975).

Acute toxicity data for inorganic selenite are available for 13 species of freshwater organisms from 10 taxonomic families (U.S. EPA 1980j). Concentrations causing acute toxicity ranged upwards by two orders of magnitude from 340 μg·L^{-1} for the scud *Hyallela azteca* (Halter *et al*. 1980). Fish are generally less sensitive to selenite than are invertebrates. The data base compiled by the U.S. EPA (1980j) for selenite and freshwater fish species has 23 values for eight species from six taxonomic families. Acute toxicity occurred at concentrations ranging from 0.6 mg·L^{-1} for the fathead minnow (*Pimephales promelas*) (Halter *et al*. 1980) to 28.5 mg·L^{-1} for the bluegill (*Lepomis macrochirus*) (Cardwell *et al*. 1976b). The 96-h LC$_{50}$

for rainbow trout (*Salmo gairdneri*) was 8 mg·L^{-1} (Hodson *et al.* 1984). The selenium concentration which caused "no effect" for developing eggs and hatched fish of rainbow trout ranged from 40 to 80 µg·L^{-1} (Davies and Goettl 1975). Green algae may be more sensitive; the lowest effect concentration was 50 µg·L^{-1} (Hutchinson and Stokes 1975).

Selenium is antagonistic to cadmium toxicity in green algae (Demayo *et al.* 1979b). It is also antagonistic to mercury, thallium and silver toxicities. Acute toxicity of selenite to the fathead minnow is directly related to water temperature (Adams 1976).

Chronic toxicity data are available for selenite from two invertebrate tests and two fish-species tests. Rainbow trout exposed to 60 and 130 µg·L^{-1} in long-term tests survived as well as control fish at the lower concentration, but exhibited elevated mortality rates and a higher incidence of deformity at the higher concentration (Goettl *et al.* 1976). Exposure of trout to selenium for 44 weeks resulted in subtle hematological responses at 28 µg·L^{-1} or higher (Hodson *et al.* 1980).

Most of the data collected by the U.S. EPA (1980j) indicate that selenite causes increasing cumulative mortality to both fish and invertebrate species with increasing time of exposure beyond the usual 4 d used in acute toxicity testing. This has also been shown by Niimi and LaHam (1975) and Halter *et al.* (1980). Bioconcentration factors have been determined for selenium in rainbow trout, fathead minnow and bluegill; they ranged from 8 to 78 (U.S. EPA 1980j). The biological half-life of selenium in rainbow trout was 29 d (Gissel-Nielson and Gissel-Nielson 1973).

The IJC (1981) introduced a numerical limit of 1 µg·L^{-1} to protect aquatic life in the Great Lakes based on field studies which indicated that waterborne selenium concentrations of 5-10 µg·L^{-1} were associated with food web contamination that caused acute lethality to predatory fish. This value has been adopted for the Canadian guideline.

3.2.1.18 Silver

3.2.1.18.1 Guideline

The concentration of total silver should not exceed 0.1 µg·L^{-1}.

3.2.1.18.2 Summary of Documents

The provinces of Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommended a numerical limit of 0.1 µg·L^{-1}, which is also the IJC (1982) limit for the Great Lakes and the limit recommended by Taylor *et al.* (1980). The U.S. EPA (1980k) established a numerical limit for total recoverable silver based on the following formula which takes water hardness into account:

$$\text{Ag conc.} = e^{(1.72[\ln(\text{hardness})] - 6.52)}\ \mu g \cdot L^{-1}$$

At water hardnesses of 50, 100 and 200 mg·L^{-1} as $CaCO_3$, the U.S. EPA (1980k) recommended that the concentration of total recoverable silver not exceed 1.2, 4.1 and 13 µg·L^{-1}, respectively, at any time.

3.2.1.18.3 Rationale

Silver is one of the most toxic metals to aquatic life. Silver nitrate and silver iodide, in particular, are very toxic. Silver chloride was 300 times less acutely toxic than the free silver ion in 30-d fathead minnow embryo-larval tests (LeBlanc *et al.* 1984). Silver thiosulphate and silver sulphide were 15 000 and 17 500 times less toxic than the free silver ion (LeBlanc *et al.* 1984). The acute toxicity of silver appears to be related to the chloride ion, but there are not enough data to develop guidelines based on chloride concentrations (U.S. EPA 1980k).

The acute toxicity of silver to aquatic organisms decreases as water hardness increases. Organic materials may also decrease the acute toxicity of silver. The U.S. EPA (1980k) compiled a data base of 82 acute values for silver exposure to 10 species from nine taxonomic families. Concentrations resulting in acute toxicity to invertebrates ranged from 0.25 µg·L^{-1} for *Daphnia magna* upwards, and to fish from 3.9 µg·L^{-1} for the fathead minnow (*Pimephales promelas*) in soft water upwards. Nebeker, McAuliffe *et al.* (1983) measured 96-h LC_{50}s for rainbow trout (*Salmo gairdneri*), steelhead trout (*Salmo gairdneri*) and the fathead minnow at 8.6, 9.2 and 5.6 µg·L^{-1}, respectively. The absence of food in tests with *Daphnia magna* caused silver to be about 10 times more toxic; the 48-h mean EC_{50} for *Daphnia magna* without food was 0.9 µg·L^{-1}, compared with 12.5 µg·L^{-1} in the test with food (Nebeker, McAuliffe *et al.* 1983). The 14-d TL_{50} for the immature mayfly *Ephemerella grandis*, less than 1 µg·L^{-1}, was also very low (Nehring 1976).

In an interlaboratory comparison study using life-cycle tests with *Daphnia magna*, the average acute toxicity concentrations for silver were lower than the average chronic toxicity concentrations, probably because food was added to the test solutions in the chronic tests, but not in the acute tests (U.S. EPA 1980k). The chronic toxicity concentration for silver derived from an early-life-stage test using rainbow trout was 0.12 µg·L^{-1} (Davies and Geottl 1978). In an early-life-stage test using steelhead trout, decreases in fish survival and mean length were significant at silver concentrations of 0.5 and 0.1 µg·L^{-1}, respectively (Nebeker, McAuliffe *et al.* 1983). The mean 21-d EC_{50} for *Daphnia magna* (with food) was 3.5 µg·L^{-1} (Nebeker, McAuliffe *et al.* 1983). No relationship has been found between chronic toxicity and water hardness.

The maximum acceptable toxicant concentration for free silver ion tested with rainbow trout (developing eggs) was greater than 0.09 µg·L^{-1}, but less than 0.17 µg·L^{-1} (Davies and Goettl 1978). The maximum acceptable toxicant concentrations for silver sulphide and silver thiosulphate complexes were greater than 11 and 16 mg·L^{-1}, respectively, but less than 35 mg·L^{-1} (LeBlanc *et al.* 1984). The differences for free silver and silver sulphide are five orders of magnitude; thus, the speciation of silver is an important factor.

Plants appear to be more resistant to silver than are some animals; therefore, guidelines to protect the most sensitive animals should also protect plants (U.S. EPA 1980k). Cell multiplication was inhibited in the blue-green alga *Microcystis aeruginosa* and the green alga *Scenedesmus quadricauda* at silver concentrations of 0.7 and 9.5 µg·L^{-1}, respectively (Bringmann and Kuhn 1978a). The growth of *Chlorella vulgaris* was retarded at a concentration of 10 µg·L^{-1} (Hutchinson and Stokes 1975). Bioconcentration factors are low, ranging from less than 1 to 240 (U.S. EPA 1980k).

The numerical limit of 0.1 µg·L^{-1} commonly recommended in Canada is adopted as the guideline, because it is supported by recent literature. The importance of the speciation of the metal, the presence of food and the effect of water hardness on acute toxicity should be considered when applying the guideline to specific locations.

3.2.1.19 Thallium

3.2.1.19.1 Guideline

There are insufficient data to recommend a guideline for thallium.

3.2.1.19.2 Summary of Documents

The U.S. EPA (1973) recommended that a concentration of 0.05 mg·L^{-1} thallium in seawater presented minimal risk to marine aquatic life. Although the literature cited in that document pertained mainly to freshwater species, no numerical limit was established for fresh water. Thallium was not included in the water quality criteria published by the U.S. EPA in 1976. The provinces of Ontario and Manitoba withdrew their numerical limits in 1982 and 1983, respectively, because of insufficient information. The U.S. EPA (1980l) prepared a document on ambient water quality criteria for thallium, but insufficient data were available to establish limits.

3.2.1.19.3 Rationale

The acute and chronic sensitivities of the invertebrate *Daphnia magna* and the fathead minnow (*Pimephales promelas*) to thallium were similar. Concentrations that were acutely and chronically toxic ranged upwards from 910 and 57 μg·L^{-1}, respectively (U.S. EPA 1980l). The LC$_{50}$s for the bluegill (*Lepomis macrochirus*) were about two orders of magnitude higher. Atlantic salmon (*Salmo salar*) is the most sensitive species that has been studied (Zitko *et al.* 1975); partial mortality occurred at exposures as low as 20 μg·L^{-1} after 100 d. The highest bioconcentration factor recorded for thallium in fish was 130 for muscle tissue of Atlantic salmon (Zitko *et al.* 1975).

Algae are also sensitive to thallium. The 96-h EC$_{50}$s for chlorophyll *a* inhibition and cell number of the alga, *Selenastrum capricornutum*, were 110 and 100 μg·L^{-1}, respectively (U.S. EPA 1978).

3.2.1.20 Zinc

3.2.1.20.1 Guideline (Tentative)

The concentration of total zinc should not exceed 0.03 mg·L^{-1}.

3.2.1.20.2 Summary of Documents

A numerical limit of 0.03 mg·L^{-1} has been established for the Great Lakes by the IJC (1976) and has also been adopted by the Province of Ontario (Ontario Ministry of the Environment 1984). The IJC is currently reviewing the zinc water quality objective for the Great Lakes. Manitoba has recently adopted a limit of 47.0 μg·L^{-1} (Williamson 1983); the U.S. EPA (1980m) established 47.0 μg·L^{-1} as a 24-h average.

EIFAC (Alabaster and Lloyd 1982) tentatively recommended that the annual 95-percentile concentration of soluble zinc should be no greater than 0.1 of the appropriate 7-d LC$_{50}$; the numerical limits depended on water hardness and type of fish (Table 3-14).

Table 3-14. Maximum Annual 95-Percentile Concentrations of Soluble Zinc (Tentative) as Recommended by EIFAC

Water hardness (mg·L^{-1} as CaCO$_3$)	95-percentile concentrations (mg·L^{-1})	
	Coarse fish (except minnows)	Salmonids
10	0.3	0.03
50	0.7	0.2
100	1.0	0.3
500	2.0	0.5

Source: Alabaster and Lloyd 1982.

Table 3-15. Water Quality Guidelines for Zinc as Recommended by Taylor and Demayo (1980)

Water hardness (mg·L^{-1} as CaCO$_3$)	Concentration of zinc (mg·L^{-1})
0-120	0.05
120-180	0.10
180-300	0.20
300	0.30

Source: Taylor and Demayo 1980.

Taylor and Demayo (1980) recommended guidelines based on water hardness; these guidelines appear in Table 3-15.

The U.S. EPA (1980m) established an instantaneous numerical limit for total recoverable zinc based on the following formula which takes water hardness into account:

$$\text{Zn conc.} = e^{(0.83[\ln(\text{hardness})] + 1.95)}\ \mu\text{g}\cdot\text{L}^{-1}$$

At water hardnesses of 50, 100 and 200 mg·L^{-1} as CaCO$_3$, the concentration of total recoverable zinc should not exceed 180, 320 and 570 μg·L^{-1}, respectively, at any time.

3.2.1.20.3 Rationale

The acute toxicity of zinc to aquatic organisms is modified by water hardness, but chronic toxicity is not (U.S. EPA 1980m). The toxicity of zinc is also influenced by the pH of the ambient water. Generally, the acute toxicity of zinc is lower in waters with a higher water hardness and a lower pH (Mount 1966; Holcombe and Andrew 1978). Other environmental factors, including low dissolved oxygen concentrations, could exert additional stress on aquatic biota. Organic matter decreases the uptake of zinc in rainbow trout (Ramamoorthy and Blumhagen 1984). The effect of other metals on zinc toxicity should always be considered; the toxicities have been shown to be additive (Brown and Dalton 1970; Marking 1977) or synergistic (Sprague 1964; Anderson and Weber 1976) depending on such factors as water hardness.

The wide range of concentrations that cause acute toxicity in fish and invertebrates, 90 μg·L^{-1} to 58.1 mg·L^{-1}, is because of hardness-related factors, biological factors such as age and size, physical-chemical factors such as temperature and (biotic) species differences (U.S. EPA 1980m). In a flow-through test, the 96-h LC$_{50}$ for rainbow trout (swim-up) was 0.093 mg·L^{-1} (Chapman 1978). The 22 96-h LC$_{50}$s for rainbow trout compiled by the U.S. EPA (1980m), however, ranged from 0.09 to 7.21 mg·L^{-1}. Similarly, the 32 96-h LC$_{50}$s for the fathead minnow ranged from 0.60 to 35.5 mg·L^{-1}. Some invertebrates are more sensitive than fish; the 48-h LC$_{50}$ for *Daphnia hyalina* was 0.04 mg·L^{-1} (Baudouin and Scoppa 1974).

Chronic toxicity generally begins at a zinc concentration of about 0.07 mg·L^{-1}. The maximum acceptable toxicant concentration in soft water ranged from 36.0 to 71.0 μg·L^{-1} for rainbow trout (fry hatching from unexposed eggs) (Goettl *et al.* 1976). The maximum acceptable toxicant concentration for the fathead minnow (spawning and hatching success and fry survival) in hard water (200 mg·L^{-1} as $CaCO_3$) ranged from 0.03 to 0.18 mg·L^{-1} (Brungs 1969), whereas the maximum acceptable toxicant concentration for fathead minnow eggs in soft water ranged from 0.078 to 0.145 mg·L^{-1} (Benoit and Holcombe 1978). A 16% reproductive impairment in *Daphnia magna* occurred after a 3-week exposure to 0.07 mg·L^{-1} (Biesinger and Christensen 1972). Growth inhibition in algae began at 0.03 mg·L^{-1} (Bartlett *et al.* 1974).

Zinc bioaccumulates, but no evidence of biomagnification was found. Accumulation of zinc by benthic organisms depends on trophic state (Rabe and Bauer 1977). Zinc concentrations are greater in benthic insects than in fish, and greater in omnivorous fish than in piscivorous species.

The numerical limit of 0.03 mg·L^{-1} is tentatively recommended. This value coincides with the measured "no-effect" concentration for rainbow trout and fathead minnows (0.036 and 0.03 mg·L^{-1}, respectively) and the beginning of growth inhibition in algae. More recent studies reported since the publications of documents reviewed for the guideline suggest that phytoplankton is more sensitive to zinc. These studies should be considered before applying this guideline for a water body where most of the zinc would be bioavailable (Taylor 1986). The guideline is not adjusted for water hardness because sufficient data are not available to show that chronic toxicity decreases as water hardness increases. Available data for the fathead minnow suggest that sensitive life stages would not be protected if the guideline were adjusted upwards.

3.2.2 Organic Parameters

3.2.2.1 Acrolein

3.2.2.1.1 Guideline

There are insufficient data to recommend a guideline for acrolein.

3.2.2.1.2 Summary of Documents

The U.S. EPA (1980n) prepared a document on ambient water quality criteria for acrolein, but the U.S. EPA's minimum data base requirements were not met. There are, therefore, no numerical limits. Acrolein has not been included in provincial, federal or EIFAC publications (Alabaster and Lloyd 1982; CCREM 1985).

3.2.2.1.3 Rationale

Acrolein has a substantially greater acute toxicity to fish than do many other herbicides used for aquatic weed control (U.S. EPA 1980n).

The relative sensitivity between different fish species and between fish and invertebrates cannot be estimated because of the different test methods used and the volatility of acrolein. The lowest toxic concentration reported by the U.S. EPA (1980n) was 90 μg·L^{-1} for the bluegill (*Lepomis macrochirus*). Rainbow trout (*Salmo gairdneri*), however, showed a 32% mortality when exposed to 48 μg·L^{-1} acrolein in a non-standard test (Bartley and Hattrup 1975). Pickering *et al.* (1983) listed 96-h LC$_{50}$ values of 80 and 70 μg·L^{-1} for rainbow trout and bluegill, respectively. The concentration of acrolein that was acutely toxic to the only species of invertebrate tested, *Daphnia magna*, was 57 μg·L^{-1} (Macek, Lindberg *et al.* 1976).

There is little apparent difference between the acute and chronic toxicities for acrolein. Chronic toxicity was observed at concentrations of 21 μg·L^{-1} for the fathead minnow and 24 μg·L^{-1} for *Daphnia magna* (U.S. EPA 1980n).

3.2.2.2 Aldrin/Dieldrin

3.2.2.2.1 Guideline

The concentration of dieldrin should not exceed 4 ng·L^{-1} in fresh water.

3.2.2.2.2 Summary of Documents

The U.S. EPA (1976) established a numerical limit of 3 ng·L^{-1} to protect freshwater aquatic life; this was later revised (U.S. EPA 1980o) to a 24-h average and an instantaneous limit of 1.9 ng·L^{-1} and 2.5 μg·L^{-1}, respectively, for dieldrin, and an instantaneous limit of 3.0 μg·L^{-1} for aldrin. The Province of Ontario (Ontario Ministry of the Environment 1984) and the IJC (1975) established a numerical limit of 1 ng·L^{-1} to protect aquatic life. The IJC also established a limit of 0.3 μg.g^{-1} in edible portions of fish to protect humans. Although the Province of Manitoba had recommended that the concentration of aldrin/dieldrin not exceed 3.0 ng·L^{-1}, it was replaced by a limit for dieldrin of 1.9 ng·L^{-1} (Williamson 1983).

3.2.2.2.3 Rationale

Aldrin is biologically altered in the environment to a more stable form, dieldrin. The toxicities of these two chemicals to a given fish species are generally very similar.

Aldrin and dieldrin are toxic to freshwater aquatic life at low concentrations. Appropriate acute toxicity values are available for 19 freshwater fish and invertebrate species representing all of the major functional and taxonomic classifications (U.S. EPA 1980o). The most sensitive fish species is the rainbow trout (*Salmo gairdneri*); the lowest 96-h LC$_{50}$ of dieldrin reported for this species was 1.1 μg·L^{-1} (Macek *et al.* 1969). The mean acute toxic concentration was 2.5 μg·L^{-1} (U.S. EPA 1980o). Invertebrates show a wide range of sensitivities to dieldrin.

The lowest concentration causing chronic toxicity was 0.22 μg·L^{-1} for rainbow trout. Some chronic values for toxicity to larval insects may be lower than those determined for fish (U.S. EPA 1980o). Plants are much more resistant.

The lipid solubility of dieldrin results in its biomagnification. Dieldrin may concentrate in an organism until it exceeds the lethal limit for a consumer. The highest bioconcentration factor reported by the U.S. EPA (1980o) was 68 286 for yearling trout. The presence of suspended solids in natural waters may reduce the actual bioconcentration (Muir *et al.* 1980).

The guideline is recommended to protect the marketability of edible fish in Canada. The method described by the U.S. EPA (1985a) has been adopted. The bioconcentration factor appears to increase with duration of exposure (U.S. EPA 1980o); therefore, the species relevant to Canada with the longest experimental exposure to dieldrin was used as recommended by the U.S. EPA (1985a). A bioconcentration factor of 68 286 for lake trout (*Salvelinus namaycush*) (U.S. EPA 1980o) which has a lipid content of approximately 11% (U.S. EPA 1985a), a standardized lipid content of 11% for freshwater fish (U.S. EPA 1985a) and the U.S. Food and Drug Administration action level of 0.3 mg·kg^{-1} have been used to derive the guideline. The guideline will also protect aquatic species from known acute and chronic toxicity.

3.2.2.3 Benzene

3.2.2.3.1 Guideline (Tentative)

The concentration of benzene should not exceed 0.3 mg·L^{-1}.

3.2.2.3.2 Summary of Documents

The U.S. EPA (1980p) prepared a document on ambient water quality criteria for benzene, but insufficient data were available to establish a numerical limit. No other guidelines pertaining to aquatic life were found.

3.2.2.3.3 Rationale

The acute toxicity of benzene to six fish species representing four families has been tested (U.S. EPA 1980p); the 96-h LC_{50} values ranged upwards from 5.3 mg·L^{-1}, the value for toxicity to rainbow trout (DeGraeve *et al.* 1982).

Fish species appear to be more sensitive than are invertebrate or plant species. Concentrations that were acutely toxic to two species of *Daphnia* were 380 and 300 mg·L^{-1} (U.S. EPA 1980p). There was a reduction in cell numbers of the alga *Chlorella vulgaris* at a benzene concentration of 525 mg·L^{-1}.

No information on chronic toxicity or measured steady-state bioconcentration factors was found.

Although limited, data are available on acute toxicity of benzene to six species of fish, including salmonid species, and two species of invertebrates. Therefore, tentative guidelines are recommended. Because chronic toxicity data are not available, an application factor of 0.05 has been applied to the lowest acute value for a freshwater species.

3.2.2.4 Chlordane

3.2.2.4.1 Guideline

The concentration of chlordane should not exceed 6 ng·L^{-1}.

3.2.2.4.2 Summary of Documents

In 1976, the U.S. EPA established a numerical limit of 0.01 μg·L^{-1} to protect aquatic life. This value was revised in 1980; to protect the marketability of edible fish, the U.S. EPA (1980q) recommended that the concentration of chlordane in water should not exceed 4.3 ng·L^{-1}. The U.S. EPA has recommended that the concentration of chlordane in water to protect aquatic life be 4.3 ng·L^{-1} as a 24-h average, and 2.4 μg·L^{-1} at any time (U.S. EPA 1980q). In 1985, the U.S. EPA recommended a change in the method of calculation (U.S. EPA 1985a) which would result in a higher concentration than that quoted in 1980.

Manitoba (Williamson 1983) recommended a limit of 4.3 ng·L^{-1}, whereas Ontario (Ontario Ministry of the Environment 1984) and the IJC (1975) recommended 60 ng·L^{-1}.

3.2.2.4.3 Rationale

Acute toxicity of chlordane to freshwater fish and invertebrate species occurs at concentrations ranging from 3 μg·L^{-1} for carp (*Cyprinus carpio*) (Rao *et al.* 1975) to 190 μg·L^{-1} for the guppy (*Poecilia reticulata*) (Henderson *et al.* 1959). Most values, including values for toxicity to four species of salmonids, fall between 15 and 60 μg·L^{-1} (U.S. EPA 1980q).

Flow-through studies on the acute and chronic toxicities of technical-grade chlordane are available (Cardwell *et al.* 1977). The 96-h LC_{50}s are 36.9, 47 and 59 μg·L^{-1} for the fathead minnow (*Pimephales promelas*), brook trout (*Salvelinus fontinalis*) and bluegill (*Lepomis macrochirus*), respectively. The 96-h EC_{50} for *Daphnia magna* was 38 μg·L^{-1}. The lowest concentration to cause a chronic effect was 0.32 μg·L^{-1}, which caused reduced embryo viability in brook trout. Effects on invertebrate species occurred at concentrations as low as 1.7 μg·L^{-1}; this concentration caused mortality of chironomid larvae in a 25-d exposure. Concentrations causing chronic toxicity to the bluegill (1.6 μg·L^{-1}) and one invertebrate species (16 μg·L^{-1}) were reported by the U.S. EPA (1980q). Chlordane concentrations ranging upwards from 0.1 μg·L^{-1} significantly stimulated cell division of *Scenedesmus quadricauda*, a common planktonic green alga (Glooschenko and Lott 1977).

Because chlordane is a highly persistent chemical which bioaccumulates in aquatic organisms used for human food, concentrations of chlordane should be kept as low as is feasible (U.S. EPA 1976). When juvenile rainbow trout were reared on diets formulated from coho salmon taken from Lake Ontario, levels of chlordane increased 10-fold over levels in fish fed control diets (Hilton *et al.* 1983).

A guideline is recommended to protect the marketability of edible fish in Canada. The method described by the U.S. EPA (1985a) has been adopted. A bioconcentration factor of 37 800 for the fathead minnow which has a lipid content of 7.6% (U.S. EPA 1980q), a standardized lipid content of 11% for freshwater fish (U.S. EPA 1985a) and the U.S. Food and Drug Administration action level of 0.3 mg·kg^{-1} have been used to calculate the guideline. Using these values, a numerical limit of 6 ng·L^{-1} is calculated. The guideline will protect aquatic species from known acute and chronic toxicities.

3.2.2.5 Chlorinated Benzenes

3.2.2.5.1 Guideline (Tentative)

The concentrations of chlorinated benzenes should not exceed those given in Table 3-16.

3.2.2.5.2 Summary of Documents

The rationale used to develop the guidelines is based on the Ontario recommendation (McCarty *et al.* 1984). It was recommended that the concentration of monochlorobenzene not exceed 15 $\mu g \cdot L^{-1}$, 1,2- and 1,3-dichlorobenzene not exceed 2.5 $\mu g \cdot L^{-1}$ and 1,4-dichlorobenzene not exceed 4.0 $\mu g \cdot L^{-1}$. Limits of 0.90, 0.50 and 0.65 $\mu g \cdot L^{-1}$ were recommended for 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene, respectively, whereas limits of 0.10, 0.10 and 0.15 $\mu g \cdot L^{-1}$ were recommended for 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene, respectively. It was recommended that the concentrations of penta- and hexachlorobenzene not exceed 30 and 6.5 $ng \cdot L^{-1}$, respectively. The Ontario Ministry of the Environment's (1984) publication included chlorinated benzenes as "substances with undefined tolerance limits." The U.S. EPA prepared documents on ambient water quality criteria for chlorinated benzenes (U.S. EPA 1980r) and dichlorobenzenes (U.S. EPA 1980s). There were insufficient data to establish numerical limits.

3.2.2.5.3 Rationale

There is a consistent direct relationship between toxicity to fish, invertebrates and plant species and the degree of chlorination of benzene. Chlorobenzene is the least toxic chlorinated benzene, with acute toxicities ranging upwards from a measured 96-h LC_{50} of 4.7 $mg \cdot L^{-1}$ for rainbow trout (*Salmo gairdneri*) (Dalich *et al.* 1982). Acute toxicities to dichlorobenzenes range upwards from a measured 96-h LC_{50} of 1.58 $mg \cdot L^{-1}$ for rainbow trout (U.S. EPA 1980s). Pentachlorobenzene is the most toxic; acute toxicities ranged upwards from a measured 12-d LC_{50} of 258 $\mu g \cdot L^{-1}$ for rainbow trout (U.S. EPA 1980r). The acute toxicity of hexachlorobenzene is difficult to determine because acute mortality for a variety of species appears to occur at or above the solubility of the compound. Water hardness does not significantly affect the toxicity of chlorobenzene (U.S. EPA 1980s).

The position of the chlorine atoms on the benzene ring does not appear to influence the toxicity of dichlorobenzenes. The range of LC_{50} values for three fish species exposed to three dichlorobenzenes was 1.12-27.0 $mg \cdot L^{-1}$. Rainbow trout appeared to be slightly more sensitive than the warm-water fish species (U.S. EPA 1980s).

No marked difference in sensitivity between fish and invertebrate species was evident from the available data, although invertebrates may be slightly more resistant (U.S. EPA 1980r). Appropriate data are available for acute toxicity to two invertebrate species and 1,2-, 1,3- and 1,4-dichlorobenzene (U.S. EPA 1980s). Concentrations ranged from 2.44 to 28.1 $mg \cdot L^{-1}$, with no consistent difference because of location of the chlorine atoms or sensitivity of the two species.

No data are available concerning the chronic toxicity of the more toxic of the chlorinated benzenes. The lowest concentration causing chronic toxicity that has been observed in a measured flow-through test was 110 $\mu g \cdot L^{-1}$ with the embryo-larval stages of rainbow trout (Black *et al.* 1982). Chronically toxic concentrations of three dichlorobenzenes ranged from 763 to 2000 $\mu g \cdot L^{-1}$ for the fathead minnow (U.S. EPA 1980s). No chronic test has been conducted with any invertebrate species. The only algal species tested (*Selenastrum capricornutum*) was less sensitive (with respect to growth and photosynthesis) than were fish (Calamari *et al.* 1983).

Table 3-16. Recommended Guidelines for Chlorinated Benzenes

Chlorobenzene		Guideline ($\mu g \cdot L^{-1}$)
Monochlorobenzene		15
Dichlorobenzene	1,2-	2.5
	1,3-	2.5
	1,4-	4.0
Trichlorobenzene	1,2,3-	0.9
	1,2,4-	0.5
	1,3,5-	0.65
Tetrachlorobenzene	1,2,3,4-	0.10
	1,2,3,5-	0.10
	1,2,4,5-	0.15
Pentachlorobenzene		0.030
Hexachlorobenzene		0.0065

Source: McCarty *et al.* 1984.

Ontario (McCarty *et al.* 1984) developed guidelines using fish acute (96-h) and early-life-stage chronic data where concentrations had been measured. Some additional data from nonstandard tests were used to assist in interpretation. Quantitative structure-activity relationships (QSAR) based on aquatic toxicity and hydrophobicity (measured by the octanol/water partition coefficients, log P_{ow}) were used to produce estimated toxicity data where experimental data were few or absent. McCarty *et al.* also used QSAR methodology to interpret and rationalize the development of the guidelines.

Bioconcentration factors correlate with degree of chlorine substitution on the benzene ring. The sequence of measured bioconcentration factors for freshwater animal species was 72 for dichlorobenzene, 182 for trichlorobenzene, 1800 for tetrachlorobenzene, 3400 for pentachlorobenzene and 22 000 for hexachlorobenzene (U.S. EPA 1980r). Tetrachlorobenzene and pentachlorobenzene are much more lipophilic than dichlorobenzene. Guidelines were not recommended in the United States because it was considered that data for each compound were limited. Many of the toxicity data that were available were based on calculated rather than measured concentrations (U.S. EPA 1980r).

3.2.2.6 Chlorinated Ethylenes

3.2.2.6.1 Guideline (Tentative)

The concentration of tetrachloroethylene should not exceed 260 $\mu g \cdot L^{-1}$. There are insufficient data to recommend guidelines for dichloroethylenes and trichloroethylene.

3.2.2.6.2 Summary of Documents

The U.S. EPA prepared documents on ambient water quality criteria for dichloroethylenes (U.S. EPA 1980t), trichloroethylene (U.S. EPA 1980u), and tetrachloroethylene

(U.S. EPA 1980v). The U.S. EPA's minimum data base requirements were not met and, hence, numerical limits were not recommended. Chlorinated ethylenes have not been included in provincial, federal (CCREM 1985) or EIFAC (Alabaster and Lloyd 1982) guidelines.

3.2.2.6.3 Rationale

There is a correlation between degree of chlorination of ethylene and toxicity. Tetrachloroethylene is more toxic than dichloroethylene. The toxicity of trichloroethylene is intermediate between the toxicities of the dichloroethylenes and tetrachloroethylene (U.S. EPA 1980t, u, v).

The position of the chlorine atoms on the dichloroethylene molecule does not appear to affect acute toxicity. The toxicities of 1,1- and 1,2-dichloroethylene are similar. Most of the acute toxicity data have been reported for 1,1-dichloroethylene and *Daphnia magna*, the fathead minnow and the bluegill. The results of one test indicated that the invertebrate, *Daphnia magna*, was the most sensitive species with an EC$_{50}$ value of 11.6 mg·L^{-1}, but results of a second test fell within the range for fish of 73.9-169.0 mg·L^{-1}. The only alga tested (*Selenastrum capricornutum*) was less sensitive to 1,1-dichloroethylene than were either fish or invertebrates (U.S. EPA 1980t).

The sensitivities of fish and invertebrates to trichloroethylene appear to be similar. The acute toxicity concentrations for exposure of two invertebrate species, *Daphnia magna* and *D. pulex*, were 64.0 and 45.0 mg·L^{-1}, respectively. The acute toxicity concentrations for two fish species, the fathead minnow and the bluegill, were 40.7 and 66.8 mg·L^{-1}, respectively. When exposed to a lower concentration, 21.9 mg·L^{-1}, the fathead minnow suffered a loss of equilibrium (U.S. EPA 1980u).

Compared with the dichloroethylenes and trichloroethylene, tetrachloroethylene is more acutely toxic to fish and invertebrate species. Acutely toxic concentrations of tetrachloroethylene to two invertebrate and three fish species ranged from 4.8 to 30.84 mg·L^{-1} (U.S. EPA 1980v). Rainbow trout was the most sensitive aquatic species; the 96-h LC$_{50}$s from two flow-through tests were 4.8 and 5.8 mg·L^{-1} (U.S. EPA 1980v). The fathead minnow and the bluegill are about as sensitive as the invertebrate, *Daphnia magna*. The alga, *Selenastrum capricornutum*, is much more resistant to tetrachloroethylene than are fish or invertebrate species, with no observed effects at concentrations as high as 816 mg·L^{-1}.

The chronic toxicity concentration of tetrachloroethylene was 840 µg·L^{-1} for the fathead minnow, the only species tested. Definitive data on chronic toxicity are not available for dichloroethylene and trichloroethylene. No chronic effects were observed for the fathead minnow at the highest concentration of dichloroethylene tested, 2.8 mg·L^{-1} (U.S. EPA 1980t). An extension of the acute toxicity test for this species showed that significant additional mortality occurred after 96 h; the LC$_{50}$ value dropped from 108 mg·L^{-1} at 96 h to 29 mg·L^{-1} at 13 d.

The bioconcentration factors for tetrachloroethylene, 49 for the bluegill and 39 for rainbow trout, were relatively low (U.S. EPA 1980v). The bioconcentration factor for trichloroethylene was 17 for the bluegill. Each had a tissue half-life of less than 1 d (U.S. EPA 1980u, v). No data are available on the bioconcentration of dichloroethylenes.

A tentative guideline for tetrachloroethylene of 260 µg·L^{-1} is recommended because acute toxicity data are available for three fish species, including a salmonid species, and two invertebrate species. Because there are no chronic data for rainbow trout, the mean acute toxicity concentration, 5.28 mg·L^{-1}, was multiplied by an application factor of 0.05.

3.2.2.7 Chlorinated Phenols

3.2.2.7.1 Guideline

The concentrations of chlorinated phenols should not exceed those given in Table 3-17.

3.2.2.7.2 Summary of Documents

The Ontario Ministry of the Environment (McKee *et al.* 1984) recommended that the concentration of monochlorophenol and dichlorophenols not exceed 7 and 0.2 µg·L^{-1}, respectively, based on flavour impairment. Limits of 18, 1 and 0.5 µg·L^{-1} were recommended for tri-, tetra- and pentachlorophenols, respectively, based on acute toxicity. The IJC (1980) recommended that the concentration of pentachlorophenol in water, also based on toxicity, should not exceed 0.4 µg·L^{-1} for the protection of aquatic life. The NRCC (1982) recommended either the banning in Canada of all uses of penta- and tetrachlorophenols or the replacement of technical-grade pentachlorophenol with tetrachlorophenol or purified products. The NRCC document does not contain recommended numerical limits.

The U.S. EPA prepared documents on ambient water quality criteria for chlorinated phenols (U.S. EPA 1980w), pentachlorophenol (U.S. EPA 1980x), 2,4-dichlorophenol (U.S. EPA 1980y) and 2-chlorophenol (U.S. EPA 1980z). Insufficient data to fulfil the U.S. EPA data requirements were available to recommend numerical limits. The U.S. EPA (1976) recommendations for phenols included references to chlorinated phenols.

3.2.2.7.3 Rationale

The rationale used to develop the guidelines is based on the Ontario recommendation (McKee *et al.* 1984). Chlorinated phenols have been shown to impair the flavour of the edible portions of fish at concentrations lower than those at which they are toxic to aquatic organisms. The highest concentration in water which would not impair the flavour of the flesh of rainbow trout (*Salmo gairdneri*) was estimated to be 1, 23, 35, 45, 52, 60 and 84 µg·L^{-1} for 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 4-chlorophenol, 2,4,6-trichlorophenol, 2-chlorophenol and 2,3-dichlorophenol, respectively (Shumway and Palensky 1973). The acute toxicity of pentachlorophenol is greater than the tainting threshold. The flavour of largemouth bass (*Micropterus salmoides*) was impaired when concentrations of 2,4-dichlorophenol exceeded 0.4 µg·L^{-1} (Shumway and Palensky 1973).

Generally, the toxicity of chlorinated phenols increases with increasing chlorine substitution, but individual compounds

Table 3-17. Recommended Guidelines for Chlorinated Phenols

Chlorophenol	Guideline[1] (µg·L^{-1})
Monochlorophenols	7
Dichlorophenols	0.2
Trichlorophenols	18
Tetrachlorophenols	1
Pentachlorophenol	0.5

[1] Guidelines are applicable to all isomers within each chlorinated class.

Source: McKee *et al.* 1984.

vary widely in toxicity. Acute toxicity values considered by the U.S. EPA were available for one invertebrate species, *Daphnia magna*, and two fish species, the fathead minnow (*Pimephales promelas*) and bluegill (*Lepomis macrochirus*). (The toxicities of pentachlorophenol and 2-chlorophenol have been determined for several additional species.) Acute toxicity for fish ranged upwards from 30 µg·L^{-1} for the fathead minnow. The range of toxicities for the invertebrate species occurred within the range for the fish species (U.S. EPA 1980w). The U.S. EPA (1980w) concluded that a single numerical limit for all chlorinated phenols was inappropriate because of the wide variability in toxicity of this group of compounds.

Pentachlorophenol appears to be more toxic than any of the lower chlorophenols. For salmonids, the 96-h LC$_{50}$ values for pentachlorophenol ranged from 31.8 to 84 µg·L^{-1} for coho salmon (*Oncorhynchus kisutch*) (Davis and Hoos 1975) and from 44 to 220 µg·L^{-1} for rainbow trout (Davis and Hoos 1975; IEC Beak Consultants Ltd. 1983). For nonsalmonids, the 96-h LC$_{50}$ values ranged from 20 to 305 µg·L^{-1} for the bluegill (Inglis and Davis 1972; Pruitt *et al.* 1977) and from 180 to 600 µg·L^{-1} for the fathead minnow (Adelman and Smith 1976; Mattson *et al.* 1976).

Invertebrate species appear to be slightly less sensitive to pentachlorophenol than are fish species; cladocerans (*Daphnia magna*, *D. pulex*, *D. cucullata*) and the snail (*Lymnaea acuminata*) with LC$_{50}$ values as low as 240 and 160 µg·L^{-1}, respectively, were the most sensitive (Canton and Adema 1978; Gupta and Rao 1982). The 96-h LC$_{50}$ values for nine oligochaete species exposed to pentachlorophenol at pH 7 and a temperature of 10°C ranged from 105 to 980 µg·L^{-1}. The oligochaetes were approximately an order of magnitude more tolerant when sediment was added to the tests (Chapman *et al.* 1982a, b).

Data from acute toxicity studies strongly suggest that pentachlorophenol is considerably more toxic at acidic than at alkaline pH. Increased temperature may also enhance toxicity (NRCC 1982).

Of the chlorophenols tested, 2-chlorophenol appeared to be the least toxic. The 96-h LC$_{50}$ values for 2-chlorophenol ranged from 2.58 to 20.17 mg·L^{-1} (U.S. EPA 1980z). A 96-h LC$_{50}$ value of 2.1 mg·L^{-1} has been reported for rainbow trout (Pulp and Paper Research Institute of Canada 1979). *Daphnia magna* was found to be the most sensitive invertebrate species, with a 48-h LC$_{50}$ value of 2.6 mg·L^{-1} (LeBlanc 1980).

Individual acute toxicity values (96-h LC$_{50}$s) of 2,4-dichlorophenol range from 1.5 mg·L^{-1} for goldfish (*Carassius auratus*) to 8.3 mg·L^{-1} for fathead minnows (*Pimephales promelas*) (Birge *et al.* 1979; Phipps *et al.* 1981). A 96-h LC$_{50}$ of 2.8 mg·L^{-1} was reported for rainbow trout (Pulp and Paper Research Institute of Canada 1979). Although the data are limited, differences between fish and invertebrate species do not appear to be significant. The 48-h LC$_{50}$ for *Daphnia magna* was 2.6 mg·L^{-1} (LeBlanc 1980). Hardness does not substantially affect toxicity (Birge *et al.* 1979). Toxicity decreases with increasing pH (Holcombe *et al.* 1982).

Short-term effects, particularly acute lethality, are mediated by chlorinated phenols directly, but effects observed after 2-3 weeks or under long-term, chronic exposure regimes are mediated by the various contaminants, especially the PCDDs (NRCC 1982).

Data on chronic effects are limited. In an embryo-larval test with fathead minnows, no adverse effects were observed at the highest test concentration of 2-chlorophenol, 3.9 mg·L^{-1} (U.S. EPA 1980z). The chronic toxicity concentrations of 2,4-dichlorophenol and 2,4,6-trichlorophenol were 365 and 720 µg·L^{-1}, respectively, for the fathead minnow (*Pimephales promelas*) (U.S. EPA 1980y; Holcombe *et al.* 1982). In a test of early life stages, the concentration of 2,4-dichlorophenol that was toxic to rainbow trout was 70 µg·L^{-1} (Holcombe *et al.* 1982).

Appropriate chronic toxicity tests with pentachlorophenol have been reported by the U.S. EPA for two freshwater species: *Daphnia magna* and the fathead minnow. Chronic toxicity concentrations were 240 and 57 µg·L^{-1}, respectively (U.S. EPA 1980x; Holcombe *et al.* 1982). The maximum acceptable toxicant concentration of pentachlorophenol for the fathead minnow in Lake Superior water was within the range of 44.9-73.0 µg·L^{-1} (Holcombe *et al.* 1982). The results of an early-life-stage test with rainbow trout showed that the lowest chronic effect (reduction in biomass) occurred at a concentration of 10 µg·L^{-1} at 20°C and 20 µg·L^{-1} at 12°C. The effect of the same concentration of PCP depended on the temperature and exposure regimes (Hodson and Blunt 1981). The observed no-effect concentration for growth responses in sockeye salmon (*Oncorhynchus nerka*) exposed to pentachlorophenol was 1.84 µg·L^{-1} (Webb and Brett 1973).

Deleterious effects on aquatic plants generally occur at concentrations much higher than those affecting aquatic animals, although data on the toxicity of chlorophenols to aquatic plants are widely divergent (Blackman *et al.* 1955; Huang and Gloyna 1968; Rosner *et al.* 1979).

Few steady-state bioconcentration factors are available for chlorinated phenols, with the exception of 2-chlorophenol and pentachlorophenol. Chlorophenols are rapidly taken up by fish, but they are also rapidly excreted (Kobayashi and Akitake 1975; Pruitt *et al.* 1977; U.S. EPA 1980x; Saarikoski and Viluksela 1982; Trujillo *et al.* 1982). Fish accumulate pentachlorophenol according to the concentration in the water and the duration of exposure (Niimi and McFadden 1982). Concentrations are usually highest in the liver and gall bladder. Bioconcentration factors for the bluegill were 214 for 2-chlorophenol (U.S. EPA 1980z), and 10 (muscle) to 350 (liver) for pentachlorophenol (Pruitt *et al.* 1977). Bioconcentration factors for rainbow trout were estimated at 240 (whole fish minus liver and gall bladder) at a constant exposure of 660 ng·L^{-1}

sodium pentachlorophenate (NaPCP) (Niimi and McFadden 1982). The bioconcentration factors for fish measured in contaminated waters ranged up to 9100 for perch (*Perca flavescens*) and 15 000 for the brown bullhead (*Ictalurus nebulosus*); the bioconcentration factors for invertebrates ranged from 60 for a chironomid to 5000 for a snail; the bioconcentration factor for the alga *Cladophora* was lower at 400 (Fox and Joshi 1984).

A guideline for pentachlorophenol of 0.5 $\mu g \cdot L^{-1}$ is recommended. The lowest mean acute toxicity concentration for salmonids, 55 $\mu g \cdot L^{-1}$ for coho salmon (Davis and Hoos 1975), was used with the application factor for persistent contaminants of 0.01. The mean acute toxicity concentration for sockeye salmon, 68 $\mu g \cdot L^{-1}$ (Johnson and Finley 1980) and 70 $\mu g \cdot L^{-1}$ for chinook salmon (*Oncorhynchus tshawytscha*) (Iwama and Greer 1979) were similar. The mean for rainbow trout was 97 $\mu g \cdot L^{-1}$ (McKee *et al.* 1984). The estimated highest no-effect concentration for growth inhibition in sockeye salmon was 1.61 $\mu g \cdot L^{-1}$ and the highest observed no-effect concentration was 1.84 $\mu g \cdot L^{-1}$ (Webb and Brett 1973). The guideline, 0.05 $\mu g \cdot L^{-1}$, should protect fish from impaired growth (McKee *et al.* 1984).

Only acute toxicity data were available for 2,3,4,6- and 2,3,5,6-tetrachlorophenol (McKee *et al.* 1984). Bluegill 96-h LC_{50} values were 140 and 170 $\mu g \cdot L^{-1}$, respectively (Buccafusco *et al.* 1981). An application factor of 0.01 for persistent chemicals was applied to give a guideline of 1 $\mu g \cdot L^{-1}$.

The bluegill was the most sensitive species to 2,4,5- and 2,4,6-trichlorophenols in terms of acute effects, with a geometric mean acute toxicity of 379 $\mu g \cdot L^{-1}$. Trichlorophenols are considered to be nonpersistent and McKee *et al.* (1984) used an application factor of 0.05 to recommend a guideline of 18 $\mu g \cdot L^{-1}$ to protect against both chronic toxicity and tainting of fish flesh. This concentration is less than half of the lowest tainting threshold.

A guideline of 0.2 $\mu g \cdot L^{-1}$ is recommended for dichlorophenols. This is one-half of 0.4 $\mu g \cdot L^{-1}$, the tainting threshold concentration of 2,4-dichlorophenol which is the most critical isomer in terms of flavour impairment (Shumway and Palensky 1973).

One-half of the lowest individual tainting threshold of 15 $\mu g \cdot L^{-1}$, i.e. 7 $\mu g \cdot L^{-1}$, is recommended as the guideline for monochlorophenols (McKee *et al.* 1984).

3.2.2.8 DDT

3.2.2.8.1 Guideline

The concentration of DDT and its metabolites should not exceed 1 $ng \cdot L^{-1}$ in fresh water.

3.2.2.8.2 Summary of Documents

The U.S. EPA's (1976) numerical limit of 1 $ng \cdot L^{-1}$ was revised in 1980 to include both a mean and an instantaneous value. The existing U.S. EPA (1980aa) limit for DDT and its metabolites is 1.0 $ng \cdot L^{-1}$ as a 24-h average and 1.1 $\mu g \cdot L^{-1}$ at any time. The U.S. EPA (1980aa) used a maximum tissue concentration of 0.15 $\mu g \cdot g^{-1}$ in fish to calculate the average values in water that would protect fish-consuming birds. The Province of Manitoba (Williamson 1983) recommended a numerical limit of 1.0 $ng \cdot L^{-1}$. The IJC (1975) and the Province of Ontario (Ontario Ministry of the Environment 1984) both recommended a limit for DDT and its metabolites of 3 $ng \cdot L^{-1}$ to protect aquatic life. The IJC (1975) stated that the concentration of DDT and its metabolites should not exceed 1.0 $\mu g \cdot g^{-1}$ (wet weight) whole fish to protect fish-consuming birds.

3.2.2.8.3 Rationale

DDT has several metabolites; the two most frequently found in nature are DDD (TDE) and DDE. DDT is intermediate in toxicity in comparison with other chlorinated hydrocarbon pesticides. It is less toxic to fish than aldrin, dieldrin, endrin and toxaphene, but more toxic than chlordane, lindane and methoxychlor (U.S. EPA 1980aa).

Generally, invertebrate species are more sensitive to DDT than are fish species. The most sensitive invertebrate tested was the 1-week-old crayfish, *Orconectes nais* (U.S. EPA 1980aa). Acute toxicity data for DDT are available for 18 freshwater invertebrate species. A wide range in species sensitivity was found, with acute toxicity occurring at concentrations ranging upwards from 0.18 $\mu g \cdot L^{-1}$ (Sanders 1972). Acute toxicity tests on 24 freshwater fish species also showed a wide range of species sensitivity, with LC_{50} values ranging from 0.6 $\mu g \cdot L^{-1}$ for yellow perch (*Perca flavescens*) (Marking 1966) to a value 300 times greater. Chronic toxicity data are available for one species only; the chronic toxicity concentration for exposure of the fathead minnow (*Pimephales promelas*) was 0.75 $\mu g \cdot L^{-1}$ (Jarvinen *et al.* 1977).

Available data for plants indicate that effects occur over a wide range of concentrations. The lowest-effect value was 0.3 $\mu g \cdot L^{-1}$ for *Chlorella* sp. (Sodergren 1968).

DDT and its metabolites are concentrated by aquatic organisms at all trophic levels. DDT enters the food web and is biomagnified (Niethammer *et al.* 1984). Bioconcentration in fish species was much greater in the field than in laboratory tests; bioconcentration factors for fish ranged from 11 607 to 4 426 666 (Reinert 1970; Miles and Harris 1973).

The recommended guideline for Canada follows the U.S. EPA (1980aa) recommendation which states that, based on a maximum permissible tissue concentration of 0.15 $\mu g \cdot g^{-1}$ for wildlife protection, the concentration of DDT in ambient water should not exceed 1 $ng \cdot L^{-1}$.

3.2.2.9 Dinitrotoluenes

3.2.2.9.1 Guideline

There are insufficient data to recommend guidelines for dinitrotoluenes.

3.2.2.9.2 Summary of Documents

The U.S. EPA (1980ab) prepared a document on ambient water quality criteria for dinitrotoluene, but the U.S. EPA's minimum data base requirements were not met and, hence, numerical limits were not recommended. No other guidelines for dinitrotoluenes pertaining to aquatic life were found.

3.2.2.9.3 Rationale

The few data that are available for freshwater organisms indicate that 2,3-dinitrotoluene is two orders of magnitude more toxic to fish and invertebrate species than is 2,4-dinitrotoluene. Fish and invertebrate species appear to be of similar sensitivity. Acute toxicity concentrations were within the range of 330-660 $\mu g \cdot L^{-1}$ for 2,3-dinitrotoluene, and 31 000-35 000 $\mu g \cdot L^{-1}$ for 2,4-dinitrotoluene (U.S. EPA 1980ab). The only alga tested, *Selenastrum capricornutum*, was less sensitive to 2,3-dinitrotoluene than were fish (U.S. EPA 1978). A chronic toxicity concentration for exposure to 2,3-dinitrotoluene of the early life stages of the fathead minnow (*Pimephales promelas*) was 230 $\mu g \cdot L^{-1}$ (U.S. EPA 1980ab). Bioaccumulation data are not available.

3.2.2.10 Diphenylhydrazine

3.2.2.10.1 Guideline

There are insufficient data to recommend a guideline for diphenylhydrazine.

3.2.2.10.2 Summary of Documents

The U.S. EPA (1980ac) prepared a document on ambient water quality criteria for diphenylhydrazine, but numerical limits were not recommended because the U.S. EPA's minimum data base requirements were not met. Diphenylhydrazine has not been included in provincial or federal guidelines (CCREM 1985).

3.2.2.10.3 Rationale

Acute toxicity data are available for one fish and one invertebrate species; toxic effects in the bluegill and *Daphnia magna* occurred at concentrations that ranged from 270 to 4100 $\mu g \cdot L^{-1}$ (U.S. EPA 1978). Data on chronic toxicity and bioaccumulation are not available.

3.2.2.11 Endosulfan

3.2.2.11.1 Guideline

The concentration of endosulfan should not exceed 0.02 $\mu g \cdot L^{-1}$.

3.2.2.11.2 Summary of Documents

The U.S. EPA (1980ad) recommended numerical limits for endosulfan of 56 $ng \cdot L^{-1}$ as a 24-h average and 0.22 $\mu g \cdot L^{-1}$ at any time, replacing an earlier value of 3 $ng \cdot L^{-1}$ for freshwater aquatic life (U.S. EPA 1976). Manitoba also recommended 56 $ng \cdot L^{-1}$, which applies to an instantaneous maximum concentration not to be exceeded at any time (Williamson 1983). The Ontario Ministry of the Environment (1984) recommended a limit of 3 $ng \cdot L^{-1}$.

3.2.2.11.3 Rationale

Endosulfan is consistently one of the most toxic pesticides tested with fish species. It is second in toxicity only to endrin in acute studies with both organophosphate and organochlorine insecticides. With invertebrate species, endosulfan had intermediate toxicity among the chlorinated hydrocarbon insecticides (U.S. EPA 1980ad).

Fish species are generally more sensitive to endosulfan than are invertebrate species. Acute (96-h LC_{50}) toxicity occurred at concentrations ranging from 1.7 $\mu g \cdot L^{-1}$ for rainbow trout (*Salmo gairdneri*) to 4.4 $\mu g \cdot L^{-1}$ for bluegill (*Lepomis macrochirus*) (Pickering and Henderson 1966; Lemke 1980; Nebeker, McCrady *et al.* 1983). Acute toxicities to invertebrate species occurred at concentrations ranging from 2.3 $\mu g \cdot L^{-1}$ for the stonefly (*Pteronarcys californica*) (Sanders and Cope 1968) to 740 $\mu g \cdot L^{-1}$ for a cladoceran (*Daphnia magna*) (Lemke 1980). The alga, *Chlorella vulgaris*, is more resistant to endosulfan than are the other freshwater organisms. Data are available for 10 fish and invertebrate species; the mean acute toxicity concentration for the most sensitive species, rainbow trout, was 0.34 $\mu g \cdot L^{-1}$ (U.S. EPA 1980ad).

The toxicity of endosulfan generally increases with increasing temperature for both fish and invertebrates. A two- to threefold increase in toxicity to rainbow trout occurred when the temperature was increased from approximately 1.5°C to about 10°C (Macek *et al.* 1969; Schoettger 1970). Water hardness had no significant effect on the toxicity of endosulfan to bluegills (Pickering and Henderson 1966).

Chronic toxicity data for fish are available only for the fathead minnow (*Pimephales promelas*); chronic toxicity occurred at a concentration of 0.28 $\mu g \cdot L^{-1}$. The acute:chronic ratio for the fathead minnow is 3. Five chronic tests with *Daphnia magna* yielded values ranging upwards from 4.3 $\mu g \cdot L^{-1}$ (Macek, Lindberg *et al.* 1976; Nebeker *et al.* 1980).

Little information is available on endosulfan bioaccumulation. Bioconcentration factors in a microcosm study ranged from 10^2-10^3 for invertebrates to 10^1-10^2 for fish (Ali 1978). Accumulation appeared to be transitory, due to rapid elimination, at least in fish (NRCC 1975).

An application factor of 0.05 and the mean acute toxicity concentration for rainbow trout of 0.34 $\mu g \cdot L^{-1}$ (U.S. EPA 1980ad), the most sensitive species, were used to derive the guideline. An application factor of 0.05 was used because there are no chronic data for rainbow trout or any other salmonids. (If the mean acute toxicity to rainbow trout were divided by three, the only acute:chronic ratio available for fish, and multiplied by a factor of 0.2, the guideline would be the same.)

3.2.2.12 Endrin

3.2.2.12.1 Guideline

The concentration of endrin in water should not exceed 2.3 $ng \cdot L^{-1}$.

3.2.2.12.2 Summary of Documents

The U.S. EPA (1980ae) recommended numerical limits of 2.3 $ng \cdot L^{-1}$ as a 24-h average and 0.18 $\mu g \cdot L^{-1}$ at any time to protect freshwater aquatic life, replacing an earlier limit of 4 $ng \cdot L^{-1}$ (U.S. EPA 1976). The Province of Manitoba (Williamson 1983) recommended 2.3 $ng \cdot L^{-1}$ as an instantaneous maximum concentration, whereas the Province of Ontario (Ontario Ministry of the Environment 1984) and the IJC (1975) recommended a limit of 2 ng·L^{-1}. The IJC (1975) also established a limit of 0.3 μg·g^{-1} in edible portions of fish to protect human consumers.

3.2.2.12.3 Rationale

Perhaps because endrin has a high acute toxicity to aquatic organisms, it was more frequently tested than related insecticides, such as chlordane, heptachlor and aldrin. Acute data are available for 28 species, including a wide variety of organisms normally performing a spectrum of community functions. The lowest mean acute toxicity concentration was 0.15 μg·L^{-1} for exposure of cutthroat trout (*Salmo clarki*) (Post and Schroeder 1971), but mean values for most species were clustered near 1.0 μg·L^{-1} (U.S. EPA 1980ae). The data are predominantly from static tests in which the toxicant concentrations were not measured and so probably underestimate true toxicity.

All of the mean acute toxicity concentrations for freshwater fish species are between 0.15 and 2.1 μg·L^{-1} (Henderson *et al*. 1959; Post and Schroeder 1971), suggesting a relatively narrow range of species sensitivity for fish. Most of the invertebrate species tested were substantially more tolerant than fish, although stoneflies (*Acroneuria pacifica*, *Pteronarcella badia*, *Pteronarcys californica*, *Claassenia sabulosa*) were comparable to fish in sensitivity (U.S. EPA 1980ae). The generally higher tolerance of the insects and related groups is unexpected, because endrin is an effective insecticide.

The plant data clearly indicate that plants are much more resistant to endrin than are animals. The lowest-effect concentration for plants was 475 μg·L^{-1} based on growth inhibition of *Anacystis nidulans* (Batterton *et al*. 1971).

An increased tolerance to endrin has been shown for a variety of aquatic species (U.S. EPA 1980ae). Where resistant populations of organisms were found, top predators were absent; this demonstrates that acquisition of resistance is costly to species most important to humans. None of the data on resistant populations was used because the guidelines must also protect unacclimated populations.

Life-cycle tests with two fish species, the fathead minnow (*Pimephales promelas*) and flagfish (*Jordanella floridae*) (Hermanutz 1978; Jarvinen and Tyo 1978), gave chronic toxicity concentrations near 0.2 μg·L^{-1}. Acute:chronic ratios were 2.2 and 3.3 for the fathead minnow and flagfish, respectively. Endrin is taken up quickly by aquatic organisms, but is also depurated quickly. Its short biological half-life (Jackson 1976) demonstrates that endrin is different from related pesticides, such as DDT.

Steady-state bioconcentration factors have been measured for several species of freshwater organisms, including algae, mussels and fish. The factor for mussels was 3000; the factors for fish ranged from 1640 to 15 000 (U.S. EPA 1980ae). Bioconcentration factors for endrin are relatively low compared with those for related insecticides, such as dieldrin.

Based on the U.S. Food and Drug Administration action level of 0.3 mg·kg^{-1} for edible fish and shellfish, the concentration of endrin in water should not exceed 15 ng·L^{-1} to protect the consumers of edible freshwater fish, both wildlife and humans (U.S. EPA 1980ae). To protect the marketability of fish oils, its concentration in water should not exceed 2.3 ng·L^{-1} (U.S. EPA 1980ae).

3.2.2.13 Ethylbenzene

3.2.2.13.1 Guideline (Tentative)

The concentration of ethylbenzene should not exceed 0.7 mg·L^{-1}.

3.2.2.13.2 Summary of Documents

The U.S. EPA (1980af) prepared a document on ambient water quality criteria for ethylbenzene, but insufficient data were available to recommend numerical limits. No other guidelines pertaining to aquatic life were found.

3.2.2.13.3 Rationale

Toxicities to four fish species and one daphnid species have been summarized by the U.S. EPA (1980af), but additional acute toxicity data are available (Johnson and Finley 1980; Buccafusco *et al*. 1981). The most sensitive species is rainbow trout; an acute toxicity to rainbow trout occurred at a concentration of 14.0 mg·L^{-1} (Johnson and Finley 1980).

Definitive data pertaining to the chronic toxicity of ethylbenzene are not available. No adverse effects were observed in the fathead minnow at the highest test concentration of 440 μg·L^{-1} (U.S. EPA 1978).

The algal species tested, *Selenastrum capricornutum*, was much more resistant than the animal species tested. No effects were observed at ethylbenzene concentrations as high as 438 mg·L^{-1} (U.S. EPA 1978). Data on the bioconcentration and biological half-life of ethylbenzene are not available.

A tentative guideline was derived using an application factor of 0.05 and the acute toxicity concentration of the most sensitive species, rainbow trout (Johnson and Finley 1980).

3.2.2.14 Halogenated Ethers

3.2.2.14.1 Guideline

There are insufficient data to recommend guidelines for halogenated ethers.

3.2.2.14.2 Summary of Documents

The U.S. EPA (1980ag) prepared a document on ambient water quality criteria for halogenated ethers, but numerical limits were not recommended because the U.S. EPA's minimum data base requirements were not met. No other guidelines pertaining to aquatic life were found.

3.2.2.14.3 Rationale

The only toxicity data for halogenated ethers, other than chloralkyl ethers, are for 4-bromophenylphenyl ether exposure of three freshwater species, the bluegill (*Lepomis macrochirus*), the fathead minnow (*Pimephales promelas*) and *Daphnia magna*. The cladoceran *Daphnia magna* is more sensitive, with an acute toxicity concentration of 360 μg·L^{-1}; the acute toxicity concentration for the bluegill, the only fish tested, was 4.94 mg·L^{-1} (U.S. EPA 1978). A value of

122 µg·L^{-1} for the fathead minnow was the only chronic toxicity concentration reported by the U.S. EPA (1978).

3.2.2.15 Heptachlor

3.2.2.15.1 Guideline

The concentration of heptachlor plus heptachlor epoxide in water should not exceed 0.01 µg·L^{-1}.

3.2.2.15.2 Summary of Documents

The U.S. EPA (1980ah) recommended a numerical limit for heptachlor of 3.8 ng·L^{-1} as a 24-h average and 0.52 µg·L^{-1} at any time. These limits replaced an earlier recommendation of 1 ng·L^{-1} (U.S. EPA 1976). The IJC (1977) numerical limit for the Great Lakes, 1 ng·L^{-1} heptachlor plus heptachlor epoxide, is similar to Ontario's, although heptachlor is listed by the Ontario Ministry of the Environment (1984) as a pesticide not actively used in the province. The Province of Manitoba replaced the limit for heptachlor of 5 ng·L^{-1} with 3.8 ng·L^{-1} (Williamson 1983). The IJC (1977) also recommended that the sum of the concentrations of heptachlor and heptachlor epoxide not exceed 0.3 µg·g^{-1} in the edible portions of fish to protect human consumers.

3.2.2.15.3 Rationale

The acute toxicity of heptachlor to 10 invertebrate and 8 fish species has been tested (U.S. EPA 1980ah). Results are from static tests in which the concentrations were not measured. Fish species are generally less sensitive than invertebrates; the lowest 96-h LC$_{50}$ value for rainbow trout (*Salmo gairdneri*) was 10.0 µg·L^{-1} (Macek *et al.* 1969), whereas the lowest 96-h LC$_{50}$ for the stonefly (*Pteronarcella badia*) was 0.9 µg·L^{-1} (Sanders and Cope 1968). Increased exposure time (from 24 to 96 h) can significantly increase the toxicity of heptachlor to invertebrates; the effect is not as pronounced in tests with fish. The limited data available suggest that the sensitivity of algae is similar to that of invertebrates and fish.

Although several studies compare the relative toxicities of heptachlor and other pesticides, no clear relationship is apparent. Water hardness has little effect on the toxicity of heptachlor to fathead minnows (*Pimephales promelas*) (U.S. EPA 1980ah). Studies pertaining to the effect of temperature do not show a clear trend; the toxicity to redear sunfish (*Lepomis macrochirus*) increases with increasing temperature (Bridges 1965), but the toxicity to rainbow trout does not change significantly (Macek *et al.* 1969).

Data on chronic toxicity are available only for the fathead minnow (*Pimephales promelas*). This species is less sensitive in acute tests than are some fish and invertebrate species. Chronic toxicity occurred at a concentration of 1.26 µg·L^{-1} (Macek, Lindberg *et al.* 1976).

Heptachlor persists in the aquatic environment. Bioconcentration factors were 9500 for heptachlor and 14 400 for heptachlor epoxide using fathead minnows as the test species (Veith *et al.* 1979). Based on the U.S. Food and Drug Administration action level of 0.3 mg·kg^{-1} for the flesh of edible fish, a lipid content of 15%, and a normalized bioconcentration factor of 5222, the average concentration of heptachlor in fresh water should not exceed 3.8 ng·L^{-1} (U.S. EPA 1980ah).

For the Canadian guideline, the concentration in fresh water recommended by the U.S. EPA (1980ah) to protect the marketability of edible fish has been recalculated. The U.S. EPA guidelines for deriving numerical limits (1985a) recommended that a lipid concentration of 11% be used for freshwater fish. Therefore, following the U.S. EPA (1985a) methods, the concentration in fresh water should not exceed 10 ng·L^{-1}. Alternatively, the guideline can be calculated from toxicity data. Because heptachlor is persistent, a factor of 0.01 is applied. The LC$_{50}$ for the most sensitive species, a stonefly, was 0.9 µg·L^{-1} (U.S. EPA 1980ah). (This value appears to be reasonable because the acute toxicities of heptachlor to three species of stonefly were similar (0.9-2.8 µg·L^{-1}).) The guideline derived from acute toxicity data is essentially the same as one derived to protect the marketability of edible fish.

3.2.2.16 Hexachlorobutadiene

3.2.2.16.1 Guideline

The concentration of hexachlorobutadiene should not exceed 0.1 µg·L^{-1}.

3.2.2.16.2 Summary of Documents

Environment Canada (1983a) recommended a guideline for hexachlorobutadiene of 0.1 µg·L^{-1} to protect aquatic life. The Province of Manitoba also adopted 0.1 µg·L^{-1} as its numerical limit (Williamson 1983).

The U.S. EPA (1980ai) prepared a document on ambient water quality criteria for hexachlorobutadiene, but did not recommend numerical limits because their minimum data base requirements were not met. No other guidelines were found.

3.2.2.16.3 Rationale

Hexachlorobutadiene is acutely toxic to fish and invertebrate species over the relatively narrow concentration range of 90-326 µg·L^{-1} (U.S. EPA 1980ai). The species tested included a snail (*Lymnaea stagnalis*), the fathead minnow (*Pimephales promelas*), rainbow trout (*Salmo gairdneri*) and bluegill (*Lepomis macrochirus*). Hexachlorobutadiene was chronically toxic to the fathead minnow at a concentration of 9.3 µg·L^{-1} (U.S. EPA 1980ai; Ahmad *et al.* 1984). A physiological change in the blood of largemouth bass (*Micropterus salmoides*) occurred at concentrations as low as 3.43 µg·L^{-1} (Laska *et al.* 1978). Bioconcentration factors measured experimentally for aquatic animals ranged from 29 for the largemouth bass to 6988 for the fathead minnow (U.S. EPA 1980ai; Ahmad *et al.* 1984). The bioconcentration factor for the green alga *Oedogonium cardiacum* was 160 (Laseter *et al.* 1976). Bioconcentration factors calculated from field data were as high as 5700 (Environment Canada 1983a). Biomagnification does not appear to be significant, possibly because depuration rates are relatively rapid (Environment Canada 1983a).

The guideline developed by Environment Canada (1983a) of 0.1 µg·L^{-1} is recommended. It is based on the known mean chronic effect concentration of 9.3 µg·L^{-1} for fish and an application factor of 0.01 which is applied because there is insufficient information to firmly establish a safe concentration (Environment Canada 1983a).

3.2.2.17 Hexachlorocyclohexanes

3.2.2.17.1 Guideline

The total concentration of hexachlorocyclohexane isomers should not exceed 0.01 $\mu g \cdot L^{-1}$.

3.2.2.17.2 Summary of Documents

The Province of Ontario (Ontario Ministry of the Environment 1984) set a limit of 0.01 $\mu g \cdot L^{-1}$. A maximum concentration of 0.02 $\mu g \cdot L^{-1}$ has recently been proposed by the IJC (1986) for total hexachlorocyclohexane isomers. Manitoba recommended a numerical limit of 0.08 $\mu g \cdot L^{-1}$ as an instantaneous maximum (Williamson 1983). The ambient water quality criteria for hexachlorocyclohexane published by the U.S. EPA (1980aj) contain instantaneous and 24-h mean numerical limits of 2.0 and 0.08 $\mu g \cdot L^{-1}$, respectively. The 1980 limits replaced the earlier (U.S. EPA 1976) recommendation of 0.01 $\mu g \cdot L^{-1}$.

3.2.2.17.3 Rationale

Generally, warm-water fish species appear to be more tolerant of lindane than are the cold-water salmonid species. The 96-h LC$_{50}$ value for brown trout (*Salmo trutta*), the most sensitive species, was 2 $\mu g \cdot L^{-1}$ (Macek and McAllister 1970). The acute (96-h LC$_{50}$) toxicity concentrations for exposure of salmonids ranged from 2 to 50 $\mu g \cdot L^{-1}$, whereas concentrations for warm-water fish ranged up to 152 $\mu g \cdot L^{-1}$ (Henderson *et al.* 1959). The U.S. EPA (1980aj) compiled data on the acute toxicity of lindane to 7 invertebrate and 15 fish species.

Invertebrates appear to have a fairly wide range of acute sensitivity to lindane (γ-isomer). The 96-h LC$_{50}$ values for the most sensitive crustacean species ranged from 10 to 15 $\mu g \cdot L^{-1}$ for *Asellus brevicaudus* and *Gammarus fasciatus* (Sanders 1972) and from 35 to 65 $\mu g \cdot L^{-1}$ for *G. lacustris* (Sanders 1969). Tadpoles of the frog (*Pseudacris triseriata*) and toad (*Bufo woodhousii*) were more resistant than warm-water fish. Although data are available for only one alga, *Scenedesmus acutus*, aquatic plants appear to be much less sensitive than fish (U.S. EPA 1980aj).

Chronic toxicity values for lindane are available for four invertebrate species (U.S. EPA 1980aj). Based on life-cycle tests, the chronic toxicity concentrations for exposure of the midge, *Chironomus tentans*, and the scud, *Gammarus fasciatus*, are 3.3 and 6.1 $\mu g \cdot L^{-1}$, respectively. The chronic toxicity concentrations for lindane exposure of the fathead minnow and *Daphnia magna* are very similar, 14.6 and 14.5 $\mu g \cdot L^{-1}$, respectively. The midge is the most sensitive species; the highest concentration of lindane that produced no observable adverse effects was 2.2 $\mu g \cdot L^{-1}$ (Macek, Buxton *et al.* 1976).

Bioconcentration factors for lindane ranged from 35 to 486 for a variety of fish species (U.S. EPA 1980aj). Biomagnification of lindane is not anticipated since depuration rates are rapid (Rodgers *et al.* 1983).

The numerical limit of 0.01 $\mu g \cdot L^{-1}$ established by the Ontario Ministry of the Environment (1979) is recommended. It is calculated from an experimentally derived application factor of 0.01 for invertebrates and the 96-h LC$_{50}$ value of 1 $\mu g \cdot L^{-1}$ for stoneflies (Snow 1958; Cope 1965). The application factor is based on acute and chronic toxicities of the midge, as determined by Macek, Buxton *et al.* (1976).

3.2.2.18 Hexachlorocyclopentadiene

3.2.2.18.1 Guideline

There are insufficient data to recommend a guideline for hexachlorocyclopentadiene.

3.2.2.18.2 Summary of Documents

The U.S. EPA (1980ak) prepared a document on ambient water quality criteria for hexachlorocyclopentadiene, but a numerical limit was not established because the U.S. EPA's minimum data base requirements were not met. No other guidelines pertaining to hexachlorocyclopentadiene were found.

3.2.2.18.3 Rationale

In static tests for acute toxicity, LC$_{50}$ values ranged from 39 $\mu g \cdot L^{-1}$ for *Daphnia magna* to 180 $\mu g \cdot L^{-1}$ for the fathead minnow (*Pimephales promelas*) (U.S. EPA 1980ak). Toxicity to the fathead minnow using a flow-through test with measured concentrations occurred at 7.0 $\mu g \cdot L^{-1}$, which was lower than the result from the static test (Spehar *et al.* 1979). The effect of water hardness, if any, was slight.

The chronic value for exposure of hexachlorocyclopentadiene to the fathead minnow was 5.2 $\mu g \cdot L^{-1}$, a concentration only slightly below the lethal concentration for that species. A bioconcentration factor for fish of less than 11 was reported (Spehar *et al.* 1979).

3.2.2.19 Monohydric and Dihydric Phenols

3.2.2.19.1 Guideline

The concentration of total phenols should not exceed 1 $\mu g \cdot L^{-1}$ to prevent the tainting of fish flesh.

3.2.2.19.2 Summary of Documents

In North America, guidelines for phenolic compounds have been established to prevent the tainting of fish flesh. The U.S. EPA's (1976) numerical limit for phenol is 1 $\mu g \cdot L^{-1}$. In 1980, the U.S. EPA did not establish a numerical limit for phenol, but advised that acute and chronic toxicities occurred at concentrations as low as 10.2 and 2.56 $mg \cdot L^{-1}$, respectively (U.S. EPA 1980al). Manitoba (Williamson 1983) and Ontario (Ontario Ministry of the Environment 1984) recommend 1 $\mu g \cdot L^{-1}$ for phenols. There is a U.S. EPA (1980am) criteria document for 2,4-dimethylphenol, but data were insufficient to establish numerical limits.

EIFAC (Alabaster and Lloyd 1982) set tentative limits for the protection of European freshwater fish. To ensure the long-term survival of salmonids in the presence of phenolic wastes, the concentrations of phenol, cresols or xylenols were not to exceed 1.0 $mg \cdot L^{-1}$, either singly or collectively. Where 2,5-xylenol is the main constituent, the concentration was not to exceed 0.5 $mg \cdot L^{-1}$. Where the temperature is lower than 5°C, concentrations may have to be halved to ensure the survival of fish. The concentrations of phenol, cresol or xylenol were limited to 2.0 mg·L^{-1}, either singly or collectively, where coarse fish were the only fish present, provided that the oxidation of the compounds at this concentration did not produce an adverse decrease in the dissolved oxygen concentration of the water. Where the temperature was lower than 5°C, it was recommended that concentrations be halved to ensure the survival of fish. To protect commercial fish from tainting, it was recommended that the concentration of xylenols not exceed 0.5 mg·L^{-1}.

3.2.2.19.3 Rationale

The toxicity of phenolic compounds varies widely with the organism tested, dissolved oxygen content and water temperature (Alabaster and Lloyd 1982). Early data on phenolic compounds are summarized in criteria documents (McKee and Wolf 1963; U.S. EPA 1973, 1976). Since that time, data for the phenolic substances of greatest interest, such as the chlorophenols and nitrophenols (see Sections 3.2.2.7 and 3.2.2.21), have been summarized in separate U.S. EPA criteria documents. Table 3-18 summarizes the recent data on acute toxicity of the remaining monohydric and dihydric compounds that have been used in developing the Canadian rationale.

Acute toxicities (48-h LC_{50}s) of phenol and beta-naphthol to invertebrates occur at concentrations that range upwards from 7.7 and 0.85 mg·L^{-1}, respectively (Lewis 1983; Millemann *et al.* 1984). The 96-h LC_{50} of 2,4-dimethylphenol for *Daphnia magna* was 2.12 mg·L^{-1} (U.S. EPA 1978).

The 96-h LC_{50} values for fathead minnows (*Pimephales promelas*) exposed to phenol and 2,4-dimethylphenol were 28.5 and 16.8 mg·L^{-1} (Phipps *et al.* 1981). Ruesinck and Smith's (1975) results for phenol using the same fish species were 36 and 24 mg·L^{-1} for males and females, respectively. Results of tests by the U.S. EPA (1978), 68 mg·L^{-1}, were higher. All tests were 96-h flow-through tests.

Salmonids appear to be more chronically sensitive to phenol than are nonsalmonids. The 27-d LC_{50}s for the eggs and larvae of rainbow trout (*Salmo gairdneri*) were 0.12 and 0.07 mg·L^{-1} for phenol and beta-naphthol, respectively (Millemann *et al.* 1984). Based on growth effects during 32-d flow-through tests, the estimated maximum acceptable toxicant concentration (MATC) for fathead minnows ranged from 1.83 to 3.57 mg·L^{-1} for phenol, and from 1.97 to 3.11 mg·L^{-1} for 2,4-dimethylphenol (Holcombe *et al.* 1982). Embryos of fathead minnows were more resistant than were larval or juvenile life stages (Holcombe *et al.* 1982). The 7-d LC_{50} for eggs and larvae of largemouth bass was 2.67 mg·L^{-1} for phenol and 1.00 mg·L^{-1} for beta-naphthol. In a life-cycle test with *Daphnia magna* (U.S. EPA 1978), the MATC for phenol was 1.5-6.3 mg·L^{-1}. Results for daphnids and fathead minnows are, therefore, similar.

Two species of aquatic mosses showed different toxic responses to phenol depending on their original habitat; concentrations of 10 mg·L^{-1} caused no effect, whereas 250 mg·L^{-1} of phenol was toxic (Samecka-Cymerman 1983).

Water-soluble fractions of a coal-liquid dispersion in which 95% of the organic carbon was present as phenols significantly reduced growth of larval fathead minnows at a concentration of 0.25 mg·L^{-1} phenolic compounds (as determined by dye photometry) (Dauble *et al.* 1983). Spawning was significantly reduced at 0.62 mg·L^{-1} (Dauble *et al.* 1983) based on partial life-cycle tests under continuous-flow regimes. Thus, the toxicity of phenolic wastes containing other compounds appears to be greater than the toxicity of pure phenol (Holcombe *et al.* 1982).

Concentrations of 1 µg·L^{-1} to protect the taste and odour of domestic water supplies and 200 µg·L^{-1} to protect fish and aquatic life were originally recommended by McKee and Wolf (1963) following a review of world literature. Pure phenol does not taint fish flesh until concentrations of 1-10 mg·L^{-1} are reached (U.S. EPA 1973), but other phenolics are more odourous. Chlorophenols, for example, taint fish at concentrations that are approximately three orders of magnitude lower (see Section 3.2.2.7).

The commonly used guideline in Canada for total phenols of 1 µg·L^{-1} is recommended, but the need for more specific guidelines is acknowledged.

3.2.2.20 Nitrobenzene

3.2.2.20.1 Guideline

There are insufficient data to recommend a guideline for nitrobenzene.

3.2.2.20.2 Summary of Documents

The U.S. EPA (1980an) prepared a document on ambient water quality criteria for nitrobenzene, but numerical limits were not established because the U.S. EPA's minimum data base requirements were not met. No other aquatic life guidelines pertaining to nitrobenzene were found.

3.2.2.20.3 Rationale

In acute toxicity tests, the 96-h LC_{50}s for *Daphnia magna*, the bluegill (*Lepomis macrochirus*) and the fathead minnow (*Pimephales promelas*) were 27.0, 43.0 and 117.0 mg·L^{-1}, respectively (LeBlanc 1980; Buccafusco *et al.* 1981; Holcombe *et al.* 1984). The 96-h EC_{50}s for the alga, *Selenastrum capricornutum*, were 42.8 and 44.10 mg·L^{-1} (U.S. EPA 1978).

In embryo-larval tests, no effects were observed in fathead minnows at nitrobenzene concentrations as high as 32.0 mg·L^{-1} (U.S. EPA 1978). Black *et al.* (1982) exposed rainbow trout embryos for 23 d, however, and measured an LC_{50} of 2 µg·L^{-1}.

Nitrobenzene is not expected to bioaccumulate or biomagnify (Lu and Metcalf 1975). This conclusion is based on a microcosm study of the fate of radiolabelled nitrobenzene. The bioconcentration factor was 15 for the fathead minnow (Veith *et al.* 1979) and 24 for the alga *Chlorella fusca* (Geyer *et al.* 1984).

3.2.2.21 Nitrophenols

3.2.2.21.1 Guideline

There are insufficient data to recommend guidelines for nitrophenols.

Table 3-18. Recent Acute Toxicity Values for Phenol

Species	Chemical	Method[1]	Time	LC_{50} (mg·L^{-1})	Reference
AMPHIPODS					
Gammarus minus	Beta-naphthol	S, M	48-h	0.85	Millemann *et al.* 1984
	Phenol	S, M	48-h	37.4	Millemann *et al.* 1984
CHIRONOMIDS					
Chironomus tentans (Midge)	Beta-naphthol	S, M	48-h	4.32	Millemann *et al.* 1984
	Phenol	S, U	48-h	187.1	Franco *et al.* 1984
		S, M	48-h	105.0	Millemann *et al.* 1984
Clinotanypus pinquis (Midge)	Phenol	S, U	48-h	80.5	Franco *et al.* 1984
Einfeldia natchitochea (Midge)	Phenol	S, U	48-h	69.8	Franco *et al.* 1984
Tanypus neopunctipennis	Phenol	S, U	48-h	70.0	Franco *et al.* 1984
CLADOCERAN					
Daphnia magna (Water flea)	2,4-Dimethylphenol	S, U	96-h	2.12	U.S. EPA 1978
	Beta-naphthol	S, M	48-h	3.54	Millemann *et al.* 1984
	Phenol	S, M	48-h	19.8	Millemann *et al.* 1984
		S	48-h	7.7	Lewis 1983
FISH					
Lepomis macrochirus (Bluegill)	2,4-Dimethylphenol	S, U	96-h	7.75	U.S. EPA 1978
Micropterus salmoides (Largemouth bass)	Beta-naphthol	FT, M	7-d	1.00	Millemann *et al.* 1984
	Phenol	FT, M	7-d	2.67	Millemann *et al.* 1984
Pimephales promelas (Fathead minnow)	2-Allylphenol	FT, U	96-h	13.2	Holcombe *et al.* 1984
	2,4-Dimethylphenol	FT, U	96-h	17.0	Phipps *et al.* 1981
	2,6-Dimethylphenol	FT, U	96-h	>27.0	Phipps *et al.* 1981
	3-Methoxyphenol	FT, U	96-h	76.0 [2]	Phipps *et al.* 1981
	1-Naphthol	FT, U	96-h	4.24	Holcombe *et al.* 1984
	Beta-naphthol	S, M	96-h	3.46	Millemann *et al.* 1984
	Nonylphenol	FT, U	96-h	0.135	Holcombe *et al.* 1984
	Phenol	FT, U	96-h	29.0 [2]	Phipps *et al.* 1981
		S, M	48-h	25.6	Millemann *et al.* 1984
		FT	96-h	36.0 m [3]	Ruesinck and Smith 1975
		FT	96-h	24.0 f [3]	Ruesinck and Smith 1975
	4-Phenylazophenol	FT, U	96-h	1.09	Holcombe *et al.* 1984
	2-Phenylphenol	FT, U	96-h	5.99	Holcombe *et al.* 1984
	4-*Tert*-butylphenol	FT, U	96-h	5.14	Holcombe *et al.* 1984
	4-*Tert*-pentylphenol	FT, U	96-h	2.50	Holcombe *et al.* 1984
	2,4,6-Tribromophenol	FT, U	96-h	6.7 [2]	Phipps *et al.* 1981
Poecilia reticulata (Guppy)	Phenol	S, M	96-h	40.0 m [3]	Colgan *et al.* 1982
		S, M	96-h	44.0 f [3]	Colgan *et al.* 1982
Salmo gairdneri (Rainbow trout)	Ortho-cresol	—	24-h	2.0	Albersmeyer and von Erichsen 1959
	Beta-naphthol	FT, M	27-d	0.07	Millemann *et al.* 1984
	Phenol	—	24-h	5.0	Albersmeyer and von Erichsen 1959
		FT, M	27-d	0.12	Millemann *et al.* 1984
MOLLUSCS					
Physa gyrina (Snail)	Beta-naphthol	S, M	48-h	24.7	Millemann *et al.* 1984
	Phenol	S, M	48-h	260.0	Millemann *et al.* 1984

[1] S = static; FT = flow-through; U = unmeasured; M = measured.

[2] Result is an average of duplicate tests.

[3] m = male; f = female.

3.2.2.21.2 Summary of Documents

The U.S. EPA (1980ao) prepared a document on ambient water quality criteria for nitrophenols, but numerical limits were not established because the U.S. EPA's minimum data base requirements were not met. No other guidelines pertaining to nitrophenols were found.

3.2.2.21.3 Rationale

The four nitrophenols for which acute toxicity data are available are 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 4-nitrophenol and 2,4,6-trinitrophenol. They are listed in decreasing order of toxicity. Acute LC_{50}s ranged upwards from 230 $\mu g \cdot L^{-1}$ for bluegills (*Lepomis macrochirus*) exposed to 2,4-dinitro-6-methylphenol (U.S. EPA 1978). Bluegills appear to be more sensitive than fathead minnows (*Pimephales promelas*) for all the nitrophenols tested. The most sensitive invertebrate species was the stonefly (*Pteronarcys californica*) exposed to an unspecified dinitromethylphenol; the LC_{50} was 320 $\mu g \cdot L^{-1}$ (Sanders and Cope 1968).

Aquatic plants appear to be more sensitive than fish or invertebrates in some instances. Studies with plants exposed to various nitrophenols showed that effects occurred at exposure concentrations ranging upwards from 150 $\mu g \cdot L^{-1}$ for 2,4-dinitro-6-methylphenol (Bringmann and Kuhn 1978a).

3.2.2.22 Phenoxy Herbicides

3.2.2.22.1 Guideline

The concentration of ester formulations of 2,4-D should not exceed 4.0 $\mu g \cdot L^{-1}$.

3.2.2.22.2 Summary of Documents

The NRCC has published two documents on 2,4-dichlorophenoxyacetic acid (2,4-D). The most recent (NRCC 1983a) addresses current issues related to the toxicity and doses of 2,4-D to humans; it does not address the toxicity to aquatic life or wildlife. An earlier document (NRCC 1978) reviewed the toxicology and bioconcentration of 2,4-D in aquatic systems. Neither document contains guidelines.

The Province of Ontario has set a limit of 4.0 $\mu g \cdot L^{-1}$ for the butoxyethanol ester (BEE) of 2,4-D (Ontario Ministry of the Environment 1984). Toxicity limits of this ester for fish were addressed by Mount and Stephan (1976).

The U.S. EPA (1976) did not establish a numerical limit to protect aquatic life; 2,4-D was not included as one of the 64 ambient water quality criteria published by the U.S. EPA in 1980.

3.2.2.22.3 Rationale

For sensitive fish and invertebrates, the 24-h and 48-h LC_{50}s of some ester formulations (e.g. PGBE, BEE, isopropyl) were less than 1 $mg \cdot L^{-1}$ (NRCC 1978). The PGBE formulations were generally most toxic to crustaceans, followed by BEE formulations. The 96-h LC_{50} for salmon (sockeye fingerlings [*Oncorhynchus nerka*], coho fry [*O. kisutch*] and pink fry [*O. gorbuscha*]) exposed to the BEE formulation of 2,4-D was approximately 0.45 $mg \cdot L^{-1}$; however, no mortality or distress was observed among sockeye fingerlings exposed to 200 $mg \cdot L^{-1}$ 2,4-D acid for 168 h (Martens *et al.* 1980). A clear stress response, as shown by interrenal (head kidney) hypertrophy, was present in sockeye fry exposed to 0.3 $mg \cdot L^{-1}$ of the BEE formulation of 2,4-D for 96 h (McBride *et al.* 1981). A limit of 4 $\mu g \cdot L^{-1}$ for the BEE formulation to protect fish has been recommended by Mount and Stephan (1976).

Rapid hydrolysis of the ester is usually assumed to minimize the duration of exposure of aquatic fauna to the esters themselves. Ester hydrolysis rates may, however, be slowed by cold temperatures and acidic conditions. There is an increased risk for the use of toxic esters in cold or acidic waters (see Section 6.3.12.3.1.4).

The acid and amine salt formulations are of much lower toxicity; the 24- and 48-h LC_{50}s may exceed 50 or 100 $mg \cdot L^{-1}$ for various fish species (NRCC 1978). Therefore, the potential hazard for fish is greatly decreased by the use of these formulations.

Algal cells do not appear to be very sensitive to 2,4-D (NRCC 1978). In various tests, common algal species showed no effect when exposed to concentrations of 2 $mg \cdot L^{-1}$. No decrease in productivity occurred in natural phytoplankton populations exposed to 1 $mg \cdot L^{-1}$ of the free acid formulation of 2,4-D (NRCC 1978).

The secondary effects of direct applications for aquatic weed control may be more significant than direct toxicity. Removal of aquatic plants by 2,4-D applications could reduce the availability of food and shelter for many invertebrates and fish. The decomposition of aquatic macrophytes could release nutrients which may stimulate algal blooms. Oxygen demand could increase as bacteria decompose the dead plants. If oxygen depletion is severe, it may cause the mortality of fish and benthic organisms. An increase in carbon dioxide and a decrease in pH may also occur. Herbicide applications early in the growing season before peak plant biomass is attained and while active growth is occurring will reduce the risk of adverse impacts on water quality.

Anticipated secondary effects may not always occur. Impacts of amine and ester formulations of 2,4-D in two experimental ponds containing Eurasian milfoil (*Myriophyllum spicatum*) were monitored over 2 years. The application rates of the 2,4-D formulations gave nominal concentrations of 1 $mg \cdot L^{-1}$ but the actual concentrations were below this during most of the study. No significant effects were observed on phytoplankton, zooplankton, dissolved oxygen or nutrients. Mortality occurred among white sucker fry (*Catostomus commersoni*) during the first few days of the first treatment year. Bacterial populations showed some increases after the collapse of the milfoil beds, and the benthic community became dominated by oligochaetes (Nagy *et al.* 1985).

Low pH and high temperatures may have an effect on 2,4-D toxicity. The synergistic effects of other pesticides on phenoxy herbicides are not well known, although the uptake of 2,4-D by rainbow trout (*Salmo gairdneri*) may be enhanced by sublethal concentrations of the carbamate insecticide, carbaryl (Statham and Lech 1976).

Short-term applications of 2,4-D can result in tainting of fish flesh. The flesh of rainbow trout exposed to 0.5 $mg \cdot L^{-1}$ of the dimethylamine salt of 2,4-D was tainted for at least 7 d after the application, even though the flesh did not contain measurable concentrations of the chemical after the first day (Folmar 1980).

A guideline of 4.0 $\mu g \cdot L^{-1}$ for ester formulations of 2,4-D is recommended based on the studies of Mount and Stephan (1976) and information summarized in NRCC (1978) that the PGBE formulation is more toxic to invertebrates than the BEE formulation.

3.2.2.23 Phthalate Esters

3.2.2.23.1 Guideline

The recommended guidelines for aquatic life are as follows:

1. DBP not to exceed 4 $\mu g \cdot L^{-1}$;
2. DEHP not to exceed 0.6 $\mu g \cdot L^{-1}$; and
3. other phthalates not to exceed 0.2 $\mu g \cdot L^{-1}$.

3.2.2.23.2 Summary of Documents

The IJC (1975) and the provinces of Manitoba (Williamson 1983) and Ontario (Ontario Ministry of the Environment 1984) have numerical limits for three categories of phthalate esters: 4 $\mu g \cdot L^{-1}$ for di-*n*-butylphthalate (DBP), 0.6 $\mu g \cdot L^{-1}$ for di-(2-ethylhexyl)phthalate (DEHP) and 0.2 $\mu g \cdot L^{-1}$ for other phthalate esters. The rationale document for Ontario's guidelines (Ontario Ministry of the Environment 1979) explains that the first two objectives were based on chronic data for daphnids (the most sensitive species) and a safety factor of 0.2. Phthalates other than the more extensively studied DBP and DEHP have been shown to be toxic, but until more information on their toxicity is available, a number of agencies recommended that in the interim, they do not exceed 0.2 $\mu g \cdot L^{-1}$. Environment Canada (1983b) guidelines for aquatic life are the same as the IJC limits. The NRCC published a review of phthalate esters with emphasis on the Canadian aquatic environment; no numerical limits, however, were recommended (Pierce *et al.* 1980).

The U.S. EPA (1973) recommended a maximum concentration of 0.3 $\mu g \cdot L^{-1}$ to protect aquatic life; this limit was recommended again in 1976. The U.S. EPA (1980ap) reviewed the water quality criteria for phthalate esters, but did not establish a numerical limit because their minimum data base requirements were not met.

3.2.2.23.3 Rationale

Phthalate esters are a diverse group of organic compounds that may not necessarily occur together in the aquatic environment. Toxicities vary with the ester tested. Appropriate acute toxicity and residue data are available for five esters; chronic toxicity data are available for two esters; and plant data are available for three esters (U.S. EPA 1980ap). The insolubility of some phthalate acid esters in water makes it difficult to determine the actual concentrations used in toxicological experiments (Pierce *et al.* 1980).

Concentrations resulting in acute toxicity, with one exception, all exceeded 1.0 $mg \cdot L^{-1}$ (U.S. EPA 1980ap). The bluegill (*Lepomis macrochirus*) is more sensitive than the fathead minnow (*Pimephales promelas*), rainbow trout (*Salmo gairdneri*) and channel catfish (*Ictalurus punctatus*), with a 96-h LC_{50} of 730 $\mu g \cdot L^{-1}$ (Mayer and Sanders 1973). The sensitivities of fish and invertebrates were generally similar.

Concentrations of butylbenzyl phthalate and DEHP, causing chronic toxicity, were as low as 220 and 3 $\mu g \cdot L^{-1}$, respectively (Mayer and Sanders 1973; Mehrle and Mayer 1976; U.S. EPA 1978; Gledhill *et al.* 1980). The most sensitive species was *Daphnia magna*. The no-effect concentration of DEHP on the early life stages of rainbow trout was between 5 and 14 $\mu g \cdot L^{-1}$ (Mehrle and Mayer 1976).

The concentrations which were toxic to algal species were similar to those for invertebrate species. Algae appeared to be the most sensitive to butylbenzyl phthalate (BBP), except for *Microcystis aeruginosa*, which was resistant (Gledhill *et al.* 1980). The concentrations of butylbenzyl phthalate toxic to algae ranged upwards from 110 $\mu g \cdot L^{-1}$ for *Selenastrum capricornutum* (U.S. EPA 1978; Gledhill *et al.* 1980).

Although aquatic organisms may accumulate phthalate esters under conditions of continuous exposure, it is unlikely that biomagnification in aquatic food webs will be significant, because efficient degradation and excretion by fish occur (Pierce *et al.* 1980). Bioconcentration factors of 155-886 were recorded for di-(2-ethylhexyl) phthalate (1.9-62 $\mu g \cdot L^{-1}$) exposure of fathead minnows (Mayer 1976). Bioaccumulation factors for mosquitofish, stickleback, minnows and bluegills lie within a similar range (Sanborn *et al.* 1975; Veith and Austin 1977; Sodergren 1982). Once exposure discontinues, depuration appears to be rapid. Di-(2-ethylhexyl) phthalate was excreted from bluegills with a half-life of 9.7-21.6 d (Mayer 1976); its primary metabolite was excreted with a half-life of 6 d (Pierce *et al.* 1980).

3.2.2.24 Polychlorinated Biphenyls (PCBs)

3.2.2.24.1 Guideline

The concentration of total PCBs in water should not exceed 1 $ng \cdot L^{-1}$.

3.2.2.24.2 Summary of Documents

The U.S. EPA (1976) recommended a numerical limit of 1 $ng \cdot L^{-1}$ for the protection of aquatic life and consumers. A recommendation that every reasonable effort should be made to minimize human exposure was included. This limit was replaced by the U.S. EPA (1980aq) value of 14 $ng \cdot L^{-1}$. It was recognized, however, that this latter value was probably too high because it was based on bioconcentration factors measured in laboratory studies.

Manitoba (Williamson 1983) and Ontario (Ontario Ministry of the Environment 1984) recommended numerical limits of 14 and 1 $ng \cdot L^{-1}$, respectively. The IJC recommended 0.1 $\mu g \cdot g^{-1}$ (wet weight) to protect fish-consuming birds and mammals (IJC 1975). The NRCC prepared a document on the biological criteria for an assessment of the effects of polychlorinated biphenyls on environmental quality; no numerical limits were, however, recommended (Roberts *et al.* 1978).

3.2.2.24.3 Rationale

The acute toxicity of PCBs appears to be similar for fish and invertebrate species under similar test conditions. Concentrations causing acute mortality, using flow-through tests, to three invertebrate species ranged from 10 $\mu g \cdot L^{-1}$ for the scud (*Gammarus fasciatus*) to 400 $\mu g \cdot L^{-1}$ for the damselfly (*Ischnura verticalis*) (Nebeker and Puglisi 1974; Mayer, Mehrle and Sanders 1977). Six 96-h flow-through tests with measured concentrations are available for fish species (Nebeker *et al.* 1974; Birge *et al.* 1979). Newly hatched fish are much more sensitive than are other life stages. Newly hatched rainbow trout (*Salmo gairdneri*) was the most sensitive species tested, with a 96-h LC_{50} of 2.0 $\mu g \cdot L^{-1}$ for a PCB containing 21%

chlorine (Birge *et al.* 1979). Largemouth bass (*Micropterus salmoides*) was also sensitive, with a 96-h LC_{50} of 2.3 $\mu g \cdot L^{-1}$ (Birge *et al.* 1979). The results of static tests are not considered, because PCBs often do not appear to be very toxic in static tests because of their low solubility.

In the 11 life-cycle and partial-life-cycle tests completed for fish and invertebrates, chronic toxicity occurred at concentrations that ranged from 0.2 to 15 $\mu g \cdot L^{-1}$ (U.S. EPA 1980aq). Chronic toxicity using flow-through tests occurred at concentrations ranging from 0.8 to 4.9 $\mu g \cdot L^{-1}$ for three invertebrate species (Nebeker and Puglisi 1974; Maki and Johnson 1975). In a 9-month continuous-flow bioassay, the spawning of fathead minnows (*Pimephales promelas*) was significantly affected at a concentration of 1.8 $\mu g \cdot L^{-1}$ Aroclor 1254 (Nebeker *et al.* 1974). Aroclor 1248 was the most toxic Aroclor (PCB) to fathead minnows at a concentration of 0.3 $\mu g \cdot L^{-1}$ (Defoe *et al.* 1978). A concentration of 1.0 $\mu g \cdot L^{-1}$ Aroclor 1254 was obtained in a chronic toxicity test with brook trout (*Salvelinus fontinalis*) (Mauck *et al.* 1978). Lake trout fry (*Salvelinus namaycush*) exposed for 6 months to concentrations of PCBs approximating resident exposure concentrations in Lake Michigan of 10 $ng \cdot L^{-1}$ in water and 1.0 $\mu g \cdot g^{-1}$ in food showed gross deformations after 1 week (Willford 1980).

PCBs depressed growth in the alga *Chlamydomonas* at concentrations ranging from 11 to 111 $\mu g \cdot L^{-1}$ (Christensen and Zielski 1980). Glooschenko and Glooschenko (1975) found that 1 $\mu g \cdot L^{-1}$ inhibited photosynthesis of phytoplankton in Lake Ontario. McNaught *et al.* (1984) found an even lower inhibition threshold of 5 $ng \cdot L^{-1}$.

PCBs are highly lipophilic and bioconcentrate to high concentrations in tissue from concentrations in water that are often below the usual detection limits (U.S. EPA 1980aq). Bioconcentration values for PCBs in invertebrates ranged up to 108 000 for the scud, *Gammarus pseudolimnaeus*, exposed for 60 d (Nebeker and Puglisi 1974). Bioconcentration factors for fish range from 3000 for brook trout (fillets) exposed to Aroclor 1254 for 500 d to 274 000 for fathead minnows (whole body) exposed to Aroclor 1242 for 255 d (Nebeker *et al.* 1974; Snarski and Puglisi 1976).

The numerical limit for the Province of Ontario is recommended as the Canadian water quality guideline. This value is based on the fact that lake trout larger than 30 cm in length from the Great Lakes generally contain more than 5 $\mu g \cdot g^{-1}$ PCBs, the U.S. Food and Drug Administration action level in fish tissue, when concentrations in the water are consistently equal to or less than 0.01 $\mu g \cdot L^{-1}$ (Ontario Ministry of the Environment 1979). PCB tissue levels as low as 2 $\mu g \cdot g^{-1}$ in fish used as animal feed affect the survival of newborn mink (Fetterolf 1975). Consumption of most Great Lakes fish and fish products decreased mink reproduction and kit survival compared with controls (Hornshaw *et al.* 1983).

The U.S. EPA (1980aq) concentration of 14 $ng \cdot L^{-1}$ is probably too high because it is based on laboratory studies. Veith *et al.* (1979) concluded that bioconcentration factors in large reservoirs and lakes such as the Great Lakes are an order of magnitude greater than laboratory-derived bioconcentration factors, although field values for small fish in rivers are similar to laboratory bioconcentration factors for fathead minnows. McNaught *et al.* (1984) recommended an objective of 5 $ng \cdot L^{-1}$ because a significant effect on phytoplankton photosynthesis occurs at that exposure concentration, but agreed that a concentration below 1 $ng \cdot L^{-1}$ must be the ultimate goal. The available data indicate that acute and chronic toxicity to aquatic life probably occurs at concentrations above those required to protect the marketability of edible fish.

3.2.2.25 Polycyclic Aromatic Hydrocarbons (PAHs)

3.2.2.25.1 Guideline

There is insufficient information to recommend guidelines for polycyclic aromatic hydrocarbons.

3.2.2.25.2 Summary of Documents

The U.S. EPA (1980ar, as) prepared documents on ambient water quality criteria for fluoranthene and polycyclic aromatic hydrocarbons with three or more rings, but insufficient data were available to recommend numerical limits. The IJC (1983) recommended that the concentration of benzo[a]pyrene in sediments or in organisms serving as a food source for fish should not exceed 1.0 $\mu g \cdot g^{-1}$, and that the concentration of benzo[a]pyrene in water should be less than 0.01 $\mu g \cdot L^{-1}$. The latter concentration was derived from the World Health Organization limit for drinking water (WHO 1984). They also noted that other 3- to 5-ring polycyclic aromatic hydrocarbons are carcinogenic and may be of equal or greater concern. No other guidelines pertaining to polycyclic aromatic hydrocarbons were found, although the Ontario Ministry of the Environment (1984) lists them as "substances with undefined tolerance limits". The NRCC (1983b) prepared a document on the formation, sources, fate and effects of polycyclic aromatic hydrocarbons on aquatic biota; no numerical limits, however, were recommended.

3.2.2.25.3 Rationale

Acute toxicity data pertaining to fluoranthene are available for one fish and one invertebrate species (U.S. EPA 1980as). The bluegill (*Lepomis macrochirus*) is more sensitive to fluoranthene than is the cladoceran, *Daphnia magna*. The 96-h LC_{50} for the bluegill was 3.98 $mg \cdot L^{-1}$ and the 48-h EC_{50} for the cladoceran was 325 $mg \cdot L^{-1}$ (U.S. EPA 1978). The 96-h EC_{50} for the alga, *Selenastrum capricornutum*, was 54.4 $mg \cdot L^{-1}$ (U.S. EPA 1978).

The U.S. EPA (1980ar) reported that no standard freshwater toxicity tests were available for any polycyclic aromatic hydrocarbon other than fluoranthene (U.S. EPA 1980as). The higher-molecular-weight PAHs were not considered highly toxic (NRCC 1983b); for example, rainbow trout (*Salmo gairdneri*) withstood the injection of up to 30 $mg \cdot kg^{-1}$ benzo[a]pyrene (Gerhart and Carlson 1978). In continuous-flow toxicity tests with embryo-larval stages of rainbow trout and largemouth bass (*Micropterus salmoides*), the LC_{50} values for phenanthrene were 0.04 and 0.18 $mg \cdot L^{-1}$, respectively (Black *et al.* 1983). In the presence of sunlight, anthracene was acutely toxic to fish at concentrations in the order of 12 $\mu g \cdot L^{-1}$ (Bowling *et al.* 1983). Histological and skeletal abnormalities were observed in rainbow trout alevins reared in aqueous solutions containing benzo[a]pyrene at concentrations as low as 0.08 $\mu g \cdot L^{-1}$ (Hose *et al.* 1984).

Benzo[a]pyrene is highly lipophilic and can bioconcentrate to high levels in some aquatic organisms. It bioaccumulates in lower organisms such as snails, but it can be degraded by higher organisms (Hallett and Brecher 1984). Bioconcentration factors for benzo[a]pyrene range from 930 in the mosquitofish (*Gambusia affinis*) to 134 240 in *Daphnia pulex* (Lu *et al*. 1977). Bioconcentration factors for anthracene range up to 3500 in the mayfly (*Hexagenia* sp.) (Herbes 1976).

The metabolic processes that prevent bioaccumulation in higher organisms convert many precarcinogenic polycyclic aromatic hydrocarbons to their ultimate carcinogenic forms. Mixtures of polycyclic aromatic hydrocarbons including benzo[a]pyrene have been found to cause tumours in fish, although the precise doses are not known (IJC 1983).

The effect of polycyclic aromatic hydrocarbons on aquatic plants is variable. At all concentrations in the range of 10-96% of saturation (up to 14 $\mathrm{mg \cdot L^{-1}}$), naphthalene stimulated growth, pyrene had no effect, and phenanthrene, fluorene, chrysene and benz[a]anthracene inhibited the growth of *Anabaena flos-aquae* (Bastian and Toetz 1982). Polycyclic aromatic compounds from coal conversion effluents caused short-term photosynthetic inhibition in the alga *Selenastrum capricornutum* (Giddings 1979).

3.2.2.26 Toluene

3.2.2.26.1 Guideline

The concentration of toluene should not exceed 0.3 $\mathrm{mg \cdot L^{-1}}$.

3.2.2.26.2 Summary of Documents

The U.S. EPA (1980at) prepared a document on ambient water quality criteria for toluene, but insufficient data were available to recommend numerical limits. No other guidelines pertaining to aquatic life were found.

3.2.2.26.3 Rationale

Concentrations of toluene causing acute toxicity to fish species ranged from 5.46 $\mathrm{mg \cdot L^{-1}}$ for coho salmon (*Oncorhynchus kisutch*) (Moles *et al*. 1981) to 240.0 $\mathrm{mg \cdot L^{-1}}$ for channel catfish (*Ictalurus punctatus*) (Johnson and Finley 1980). Acute toxicity data are also available for the fathead minnow (*Pimephales promelas*), goldfish (*Carassius auratus*), bluegill (*Lepomis macrochirus*) and rainbow trout (*Salmo gairdneri*) (Pickering and Henderson 1966; Brenniman *et al*. 1976; Johnson and Finley 1980; Buccafusco *et al*. 1981; Devlin *et al*. 1982). Subchronic toxic effects were observed in an embryo-larval study of fathead minnows at a toluene concentration of 6.0 $\mathrm{mg \cdot L^{-1}}$, but not 4.0 $\mathrm{mg \cdot L^{-1}}$ (Devlin *et al*. 1982). The threshold concentration for sublethal effects of toluene on the growth of coho salmon fry was between 0.4 and 5.8 $\mu\mathrm{g \cdot L^{-1}}$ (Moles *et al*. 1981).

Chronic toxicity of toluene to aquatic invertebrates may occur at concentrations below 4.3 $\mathrm{mg \cdot L^{-1}}$ (Syracuse Research Corporation 1983). Two freshwater algal species have been exposed to toluene; they were relatively insensitive compared with fish. There was a 50% reduction in cell numbers of the alga, *Chlorella vulgaris*, at a toluene concentration of 245.0 $\mathrm{mg \cdot L^{-1}}$ (Kauss and Hutchinson 1975).

The Ontario Ministry of the Environment (1977) found that toluene was concentrated in fish flesh by factors ranging from 57 to 6000. The alga *Chlorella fusca* concentrated toluene by a factor of 380 (Geyer *et al*. 1984).

Toluene may cause objectionable odours in fish flesh (Ogata and Miyake 1973), but the threshold concentrations in water that may cause tainting are unknown.

The guideline for the protection of aquatic life was derived using the LC$_{50}$ value of 5.46 $\mathrm{mg \cdot L^{-1}}$ for coho salmon and an application factor of 0.05.

3.2.2.27 Toxaphene

3.2.2.27.1 Guideline

The concentration of toxaphene should not exceed 8 $\mathrm{ng \cdot L^{-1}}$.

3.2.2.27.2 Summary of Documents

The IJC (1985) and Ontario (Ontario Ministry of the Environment 1984) limits are both 8 $\mathrm{ng \cdot L^{-1}}$. An objective of 0.2 $\mathrm{ng \cdot L^{-1}}$ has recently been recommended by the IJC (1986) for the protection of human consumers of fish. The U.S. EPA (1980au) established a numerical limit of 13 $\mathrm{ng \cdot L^{-1}}$ as a 24-h average and 1.6 $\mu\mathrm{g \cdot L^{-1}}$ as an instantaneous concentration. These values replaced an earlier limit of 5 $\mathrm{ng \cdot L^{-1}}$ for fresh water (U.S. EPA 1976). The Manitoba numerical limit, 13 $\mathrm{ng \cdot L^{-1}}$, is similar to the U.S. EPA value for a 24-h average, but it is an instantaneous maximum concentration not to be exceeded at any time (Williamson 1983).

3.2.2.27.3 Rationale

The U.S. EPA (1980au) compiled acute toxicity data pertaining to toxaphene for 11 invertebrate and 18 fish species. Concentrations resulting in acute toxicity to invertebrate species ranged upwards from 1.3 $\mu\mathrm{g \cdot L^{-1}}$ for the stonefly (*Claassenia sabulosa*) (Sanders and Cope 1968). Mean acute toxicity concentrations for exposure of fish species ranged upwards from 2 $\mu\mathrm{g \cdot L^{-1}}$ for largemouth bass (*Micropterus salmoides*) (Macek and McAllister 1970). When the relative susceptibilities of 12 species of fish in five families are compared, the 4 most sensitive species are from four different families: they are largemouth bass, brown trout (*Salmo trutta*), carp (*Cyprinus carpio*) and bullhead (*Ictalurus melas*) (Macek and McAllister 1970). Prolonged exposure for 34 d in flow-through tests produced a time-independent concentration of 0.6 $\mu\mathrm{g \cdot L^{-1}}$ for exposure of toxaphene to the bluegill, significantly lower than the 96-h LC$_{50}$ of 2.6 $\mu\mathrm{g \cdot L^{-1}}$ (Johnson and Julin 1980). Toxicity was not influenced by variations in pH or water hardness (Johnson and Julin 1980).

The U.S. EPA (1980au) reported chronic toxicity concentrations for three invertebrate and two fish species; concentrations ranged from 0.037 $\mu\mathrm{g \cdot L^{-1}}$ for the fathead minnow (*Pimephales promelas*) to 1.8 $\mu\mathrm{g \cdot L^{-1}}$ for the midge (*Chironomus plumosus*) (Mayer, Mehrle and Dwyer 1977; Sanders 1980). Maximum acceptable toxicant concentrations of toxaphene for three species of aquatic invertebrates (using reproduction of the daphnid, growth of the scud and emergence of the midge as indicators of toxic effects) were 0.07-0.12 $\mu\mathrm{g \cdot L^{-1}}$

for *Daphnia magna*, 0.13-0.25 $\mu g \cdot L^{-1}$ for *Gammarus pseudolimnaeus* and 1.0-3.2 $\mu g \cdot L^{-1}$ for *Chironomus plumosus* (Sanders 1980).

The maximum acceptable toxicant concentration of toxaphene for growth of brook trout (*Salvelinus fontinalis*) fry was below 39 $ng \cdot L^{-1}$ after 90 d of exposure (Mayer *et al.* 1975). The no-effect concentrations for fry growth and bone quality of fathead minnows were below 54 and 97 $ng \cdot L^{-1}$, respectively (Mayer, Mehrle and Dwyer 1977). The life stage of channel catfish (*Ictalurus punctatus*) most sensitive to toxaphene poisoning was the swim-up fry (Johnson and Julin 1980). Behavioural, macro- and microscopic changes occurred in carp fry at a toxaphene concentration of 1.0 $mg \cdot L^{-1}$ (Lakota *et al.* 1983).

Concentrations of 0.1-1.0 $mg \cdot L^{-1}$ inhibited cell numbers of the alga, *Scenedesmus quadricauda* (Stadnyk *et al.* 1971). A single EC_{50} of 0.38 $\mu g \cdot L^{-1}$ is available for the alga, *Selenastrum capricornutum* (U.S. EPA 1980au).

Toxaphene is bioaccumulated by a wide variety of organisms; it undergoes significant bioaccumulation and trophic transfer within the Great Lakes ecosystem (Rice and Evans 1984). Bioconcentration factors for toxaphene in freshwater fish species ranged from 9000 to 19 000 for rainbow trout, 4800 to 8000 for Atlantic salmon (*Salmo salar*) and averaged 15 000 in brook trout (*Salvelinus fontinalis*) (IJC 1985). To protect the marketability of fish for human consumption, the U.S. EPA (1980au) recommended that the concentration of toxaphene in the water should not exceed 76 $ng \cdot L^{-1}$. This value is higher than the maximum acceptable toxicant concentration for brook trout fry (Mayer *et al.* 1975; Mayer, Mehrle and Dwyer 1977); therefore, the Canadian guideline is based on chronic toxicity rather than bioaccumulation.

The Ontario numerical limit of 8 $ng \cdot L^{-1}$ is recommended as the Canadian guideline. It is based on the results of Mayer *et al.* (1975) and the application of a safety factor of 0.2.

3.2.3 Physical Parameters

3.2.3.1 Temperature

3.2.3.1.1 Guideline

1. Thermal Stratification

Thermal additions to receiving waters should be such that thermal stratification and subsequent turnover dates are not altered from those existing prior to the addition of heat from artificial origins.

2. Maximum Weekly Average Temperature

Thermal additions to receiving waters should be such that the maximum weekly average temperature is not exceeded.

a) In the warmer months, the maximum weekly average temperature (MWAT) is determined by adding to the physiological optimum temperature (usually for growth) a factor calculated as one-third of the difference between the ultimate upper incipient lethal temperature and the optimum temperature for the most appropriate life stage of the sensitive important species that normally is found at that location and time. Some MWAT values are shown in U.S. EPA (1976).

b) In the colder months, the MWAT is an elevated temperature that would still ensure that important species would survive if the temperature suddenly dropped to the normal ambient temperature. The limit is the acclimation temperature minus 2°C when the lower lethal threshold temperature equals the ambient water temperature.

c) During reproductive seasons, the MWAT meets specific site requirements for successful migration, spawning, egg incubation, fry rearing and other reproductive functions of important species.

d) At a specific site, the MWAT preserves normal species diversity or prevents undesirable growths of nuisance organisms.

3. Short-term Exposure to Extreme Temperature

Thermal additions to receiving waters should be such that the short-term exposures to maximum temperatures as calculated in a) and b) are not exceeded. Exposures should not be so lengthy or frequent as to adversely affect the important species.

a) For growth, the short-term maximum temperature is the 24-h median tolerance limit, minus 2°C, at an acclimation temperature approximating the MWAT for that month.

b) The short-term maximum temperature for the season of reproduction should not exceed the maximum incubation temperature for successful embryo survival, or the maximum temperature for spawning.

3.2.3.1.2 Summary of Documents

Ontario (Ontario Ministry of the Environment 1984) states that "The natural regime of any body of water shall not be altered so as to impair the quality of the natural environment. The temperature at the edge of the mixing zone shall not exceed the natural ambient water temperature by more than 10°C (18°F). Special circumstances may require a lower temperature difference."

The IJC (1976) limits for the Great Lakes consist of a maximum weekly average temperature calculated to ensure growth, reproduction and winter survival of important aquatic species, and a maximum short-term exposure to extreme temperature. It has been recommended that additions should not alter thermal stratification or turnover dates.

Manitoba (Williamson 1983) recommended that temperature limits should be site-specific, and consist of a maximum weekly average temperature calculated to ensure growth, reproduction and winter survival of important species, a time-dependent maximum temperature for short exposures and a maximum limit for temperature fluctuations. It has been recommended that thermal additions not alter thermal stratification, turnover dates, species diversity or levels of nuisance growths of aquatic plants. The U.S. EPA (1976) values regarding temperature are also similar to those in the preceding statements, although the maximum temperatures for short exposures are defined more rigidly. Many of the concepts included in the current guidelines were recommended earlier by the U.S. EPA (1973).

The tentative temperature guidelines recommended by EIFAC (Alabaster and Lloyd 1982) to protect European inland fisheries are divided into three seasons. During autumn and winter, an increase of 2°C above normal would be damaging to the reproduction of whitefish (*Coregonus* sp.) and burbot (*Lota lota*). A rise of 5-6°C increases the mortality of other salmonid embryos and fry; it may also stimulate early spring spawning in pike (*Esox lucius*), percids and cyprinids. During the spring, the optimum range of temperatures for spawning and embryonic development is no greater than 8°C. During the summer, the growth rate of bream (*Abramis brama*), white bream (*Blicca bjoerkna*) and rudd (*Scardinius erythrophthalmus*) (cyprinids) is reduced above 28°C. The upper permissible temperature for salmon and trout waters should be 20-21°C, although natural waters may rise above this temperature. Coregonids (except embryos) can withstand a rise of temperature of 5-6°C, but the sustained maximum should not exceed 22-23°C. It is reasonable to expect that an increase in temperature of 5°C to a maximum no greater than 23°C would destroy salmonid populations except for some species of *Coregonus*, and an increase of 8°C to a maximum no greater than 30°C would favour a preponderance of some cyprinids.

3.2.3.1.3 Rationale

The effects of temperature on aquatic organisms have been the subject of a number of comprehensive literature reviews (Brett 1956; Fry 1967; Kennedy and Mihursky 1967; Raney and Menzel 1967; Federal Water Pollution Control Administration 1968; Kinne 1970; Houston 1982) and annual reviews of the U.S. Water Pollution Control Federation.

Temperature changes in water bodies can alter the existing aquatic community. For example, algal predominance changes from diatoms to green algae and then to blue-green algae as water temperature increases (Cairns 1956), and fisheries change from cold- to warm-water fisheries as temperature becomes lethal, reduces activity, changes behaviour or limits reproduction (Brett 1960). Chronic exposure to slightly elevated temperature in organically enriched waters will generally cause an increase in productivity (Dickson 1975). Decreases in species diversity have also been observed. The upper tolerance limit for a balanced benthic population structure is usually higher than limits for fish, but benthic fauna are not able to move out of zones which reach intolerable levels (Federal Water Pollution Control Administration 1968; Dickson 1975).

Considerable data are available for temperature limits for fish, particularly upper limits (U.S. EPA 1973, 1976). The tolerance of organisms to extremes of temperature is a function of their genetic ability to adapt to thermal changes, the acclimation temperature prior to exposure and the time of exposure (Coutant 1972). Available data indicate that organisms subject to stress from toxic substances are less tolerant to temperature extremes (De Sylva 1969).

The effects of sublethal temperatures on metabolism, respiration, behaviour, distribution, migration, feeding rate, growth and reproduction have been summarized by De Sylva (1969). There are also more restrictive ranges for normal activity and normal reproduction in fish (Brett 1960). Different temperature conditions are required at different times of the year to meet the needs of different life stages of the fish. For example, the eggs and larvae of salmonids and coregonids are extremely sensitive to elevated temperatures. Natural temperature changes are necessary to induce the reproductive cycles of aquatic organisms and to regulate other factors (Mount 1969). A change in the natural temperature regime produces changes in the composition of aquatic communities and behaviour of aquatic species (Alabaster and Lloyd 1982).

The NRCC (Dickson 1975) assessment of waste heat in the Canadian aquatic environment concluded that a one-number guideline for the protection of aquatic life would not be feasible. The guideline currently recommended follows those adopted by the IJC, the U.S. EPA and Manitoba.

3.2.3.2 Total Suspended Solids

3.2.3.2.1 Guideline

Suspended solids should not exceed 10 mg·L^{-1} when background suspended solids concentrations are equal to or less than 100 mg·L^{-1}. Suspended solids should not exceed 10% of background concentrations when background concentrations are greater than 100 mg·L^{-1}.

3.2.3.2.2 Summary of Documents

The Ontario Ministry of the Environment (1984) recommended that suspended matter should not be added to surface water in concentrations that will change the natural Secchi disc reading by more than 10%. The British Columbia Ministry of Environment (Singleton 1985) recommendations for suspended solids state that induced nonfilterable residue should not exceed 10 mg·L^{-1} when background nonfilterable residue is equal to or less than 100 mg·L^{-1}, nor should induced nonfilterable residue be more than 10% of background when background is greater than 100 mg·L^{-1}.

Manitoba recommended that water should be free from materials that produce turbidity in such a degree as to be objectionable or to impair any beneficial use (Williamson 1983). Manitoba also has a maximum acceptable concentration for nonfilterable residue of 25 mg·L^{-1}. The Great Lakes (IJC 1978b) water quality objectives combine both a general statement and the Ontario approach.

EIFAC (Alabaster and Lloyd 1982) recommended tentative water quality guidelines for finely divided solid matter to maintain freshwater fisheries (Table 3-19). In addition, EIFAC recommended that temporary high concentrations should be prevented in rivers where good fisheries are to be maintained, even though several thousand milligrams of solids per litre may not kill fish during exposures of several hours or days. The U.S. EPA (1973) relied on the EIFAC (1965) recommendations in establishing maximum concentrations of suspended solids.

Suspended solids usually restrict light penetration in the water column. This optical property of suspended solids has been used to establish guidelines. The U.S. EPA (1973) recommended that the combined effect of colour and turbidity

Table 3-19. EIFAC and U.S. EPA Guidelines for Suspended Solids

Maximum concentration (mg·L^{-1})	Type of fisheries	Level of protection
<25	No harmful effects	High
25-80	Good or moderate fisheries	Moderate
80-400	Good fisheries unlikely	Low
>400	Poor fisheries at best	Very low

Source: EIFAC 1965; U.S. EPA 1973.

should not change the compensation point more than 10% from its seasonally established norm, nor should such a change place more than 10% of the biomass of photosynthetic organisms below the compensation point. The U.S. EPA (1976) recommended that settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10% from the seasonally established norm for aquatic life. One disadvantage of this approach is that the U.S. EPA (1976) value requires a seasonally established norm for the compensation point which may be difficult to establish reliably in waters with high variability. Secondly, the use of numerical limits based on a "compensation point" is difficult where the water is so clear and shallow that light naturally penetrates to the bottom (Thurston *et al.* 1979).

3.2.3.2.3 Rationale

In a review of the effects of suspended solids on freshwater biota for the U.S. EPA, Sorensen *et al.* (1977) pointed out that acute effects on specific organisms were difficult to demonstrate; succession and/or adaptation can allow communities to be maintained even though specific organisms differ. They concluded, however, that suspended solids may have significant effects on succession because of shading, abrasive action, habitat alteration and sedimentation. Suspended solids have a significant effect on community dynamics when they interfere with light transmission. The role of sediments as a reservoir of toxic chemicals has been demonstrated. Relatively high concentrations of suspended solids are needed to cause behavioural reactions or death in a short time in fish. Recovery is fairly rapid when fish are returned to clear water (Levings 1982).

Most flowing waters have considerable variation in suspended solids from day to day. Because this natural variation is so great, it is not desirable to establish fixed rigid guidelines (Sorenson *et al.* 1977).

Lloyd (1985) concluded that an increase in turbidity of 25 NTU (Nephelometric Turbidity Units) in shallow, clear-water systems may potentially reduce stream primary productivity by 13-50% or more, and be associated with an increase in suspended sediment concentration of approximately 25-100 mg·L^{-1}. A 5 NTU increase in turbidity in clear-water systems may reduce the primary productivity volume of lakes by approximately 75%, reduce stream productivity by 3-13% or more and be associated with an increase in suspended sediment concentration of approximately 5-25 mg·L^{-1}.

McLeay *et al.* (1984) completed a comprehensive study of the direct effects on salmonids using arctic grayling (*Thymallus arcticus*) and placer mine sediments from the Yukon Territory. At suspended sediment concentrations of 100 mg·L^{-1} or greater, fish growth was depressed and feeding responses were slower. At concentrations of 300 mg·L^{-1} or greater, fish were displaced downstream, oxygen uptake rates were increased and fish tolerance to a toxicant was reduced. Langer (1980) found that a marked reduction in survival of chum salmon eggs (*Oncorhynchus keta*) occurred at a suspended sediment concentration of 97 mg·L^{-1}. A reduction in the feeding of juvenile coho salmon (*Oncorhynchus kisutch*) occurred at 300 mg·L^{-1} (Noggle 1978).

The most recent Canadian research (Singleton 1985) and numerical limits recommended by British Columbia were used in preparing the Canadian guideline.

3.3 REFERENCES

Abelovich, A. and Y. Azov. 1976. Toxicity of ammonia to algae in sewage oxidation ponds. Appl. Environ. Microbiol. 31: 801-806.

Adams, W.J. 1976. The Toxicity and Residue Dynamics of Selenium in Fish and Aquatic Invertebrates. Ph.D. dissertation. Dep. of Fisheries and Wildlife, Michigan State University, East Lansing, Michigan.

Adelman, I.R. and L.L. Smith, Jr. 1976. Fathead minnows, *Pimephales promelas*, and goldfish, *Carassius auratus*, as standard fish in bioassays and their reaction to potential reference toxicants. J. Fish. Res. Board Can. 33: 209-214. (Cited in McKee *et al.* 1984.)

Ahmad, N., D. Benoit, L. Brooke, D. Call, A. Carlson, D. DeFoe, J. Huot, A. Moriarity, J. Richter, P. Schubat, G. Veith and C. Wallbridge. 1984. Aquatic Toxicity Tests to Characterize the Hazard of Volatile Organic Chemicals in Water: A Toxicity Data Summary. Parts 1 and 2. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-84-009.

Alabaster, J.S. and R. Lloyd. 1982. Water Quality Criteria for Freshwater Fish. 2nd edition. Food and Agriculture Organization of the United Nations. Butterworths, London. 361 pp.

Albersmeyer, W. and L. von Erichsen. 1959. Untersuchungen zur wirkung von teerbestandteilen in abwässern. Z. Fisch. 8: 29-39.

Alberta Ministry of the Environment. 1977. Surface Water Quality Objectives. Water Quality Branch, Standards and Approvals Division, Edmonton, Alberta.

Ali, S. 1978. Degradation and Environmental Fate of Endosulfan Isomers and Endosulfan Sulfate in Mouse, Insect and Laboratory Model Ecosystem. Ph.D. Thesis. Univ. Illinois. Univ. Microfilms, Ann Arbor, Michigan. No. 78-20891. (Diss. Abstr. Int. B 1978, 39(5): 2117.) (Cited in U.S. EPA 1979.)

Anderson, K.B., R.E. Sparks and A.A. Paparo. 1978. Rapid Assessment of Water Quality Using the Fingernail Clam, *Musculium transversum*. Water Resources Center, University of Illinois, Urbana, Illinois. WRC Res. Rep. No. 133. 115 pp.

Anderson, P.D. and L.J. Weber. 1975. The toxicity to aquatic populations of mixtures containing certain heavy metals. *In* Proc. Int. Conf. on Heavy Metals in the Environment, Toronto, Ontario. Vol. II. Part 1. pp. 933-953.

Anderson, P.D. and L.J. Weber. 1976. The multiple toxicity of certain heavy metals; additive actions and interactions. *In* Toxicity to Biota of Metal Forms in Natural Waters. R.W. Andrew, P.V. Hodson and D.E. Konasewich (eds.). Great Lakes Advisory Board, International Joint Commission, Windsor, Ontario. pp. 263-282.

Anonymous. 1980. Part V. Environmental Protection Agency. Water quality criteria documents; availability. Fed. Regist. 45: 79318-79379.

Arillo, A., E. Gaino, C. Margiocco, P. Mensi and G. Schenone. 1984. Biochemical and ultrastructural effects of nitrite in rainbow trout: liver hypoxia as the root of the acute toxicity mechanism. Environ. Res. 34: 135-154.

Arthur, J.W. and J.G. Eaton. 1971. Chloramine toxicity to the amphipod *Gammarus pseudolimnaeus* and the fathead minnow (*Pimephales promelas*). J. Fish. Res. Board Can. 28: 1841-1845.

Arthur, J.W., R.W. Andrew, V.R. Mattson, D.T. Olson, G.E. Glass, B.J. Halligan and C.T. Walbridge. 1975. Comparative Toxicity of Sewage-effluent Disinfection to Freshwater Aquatic Life. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-75-012.

Atchison, G.J., B.R. Murphy, W.E. Bishop, A.W. McIntosh and R.A. Mayes. 1977. Trace metal contamination of bluegill (*Lepomis macrochirus*) from two Indiana lakes. Trans. Am. Fish. Soc. 106: 637-640.

Baker, J.P. and C.L. Schofield. 1982. Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut. 18: 289-309.

Bartlett, L., F.W. Rabe and W.H. Funk. 1974. Effects of copper, zinc and cadmium on *Selanastrum capricornutum*. Water Res. 8: 179-185.

Bartley, T.R. and A.R. Hattrup. 1975. Acrolein Residues in Irrigation Water and Effects on Rainbow Trout. Bureau of Reclamation, U.S. Dep. of the Interior, Washington, D.C. Rep. REC-ERC-75-8.

Bastian, M.V. and D.W. Toetz. 1982. Effect of eight polynuclear hydrocarbons on growth of *Anabaena flos-aquae*. Bull. Environ. Contam. Toxicol. 29: 531-538.

Batterton, J.C., G.M. Boush and F. Matsumura. 1971. Growth response of blue-green algae to aldrin, dieldrin, endrin and their metabolites. Bull. Environ. Contam. Toxicol. 6: 589-594.

Baudouin, M.F. and P. Scoppa. 1974. Acute toxicity of various metals to freshwater zooplankton. Bull. Environ. Contam. Toxicol. 12: 745-751.

Bell, H.L. 1971. Unpublished data. National Water Quality Laboratory, Duluth, Minnesota. (Cited in U.S. EPA 1973.)

Benoit, D.A. 1976. Toxic effects of hexavalent chromium on brook trout (*Salvelinus fontinalis*) and rainbow trout (*Salmo gairdneri*). Water Res. 10: 497-500.

Benoit, D.A. and G.A. Holcombe. 1978. Toxic effects of zinc on fathead minnows *Pimephales promelas* in soft water. J. Fish Biol. 13: 701-708.

Benoit, D.A., E.N. Leonard, G.M. Christensen and J.T. Fiandt. 1976. Toxic effects of cadmium on three generations of brook trout (*Salvelinus fontinalis*). Trans. Am. Fish. Soc. 105: 550-560.

Biesinger, K.E. and G.M. Christensen. 1972. Effects of various metals on survival, growth, reproduction and metabolism of *Daphnia magna*. J. Fish. Res. Board Can. 29: 1690-1700.

Biesinger, K.E., L.E. Anderson and J.G. Eaton. 1982. Chronic effects of inorganic and organic mercury on *Daphnia magna*: toxicity, accumulation, and loss. Arch. Environ. Contam. Toxicol. 11: 769-774.

Birge, W.J. 1978. Aquatic toxicology of trace elements of coal and fly ash. *In* Energy and Environmental Stress in Aquatic Systems. J.H. Thorpe and J.W. Gibbons (eds.). Technical Information Service Center, Springfield, Virginia. pp. 219.

Birge, W.J. and J.A. Black. 1979. Effect of copper on embryonic and juvenile stages of aquatic animals. *In* Copper in the Environment. Part 2. J.O. Nriagu (ed.). John Wiley & Sons, New York. pp. 373-399.

Birge, W.J., J.A. Black and D.M. Bruser. 1979. Toxicity of Organic Chemicals to Embryo-larval Stages of Fish. U.S. Environmental Protection Agency. EPA-560/11-79-007.

Birge, W.J., J.A. Black, A.G. Westerman and J.E. Hudson. 1980. Aquatic toxicity test on inorganic elements occurring in oil shale. *In* Oil Shale Symposium: Sampling, Analysis and Quality Assurance. March 26-28, 1979, Denver, Colorado. C. Gale (ed.). pp. 519-534. NTIS PB80-221435. (Cited in U.S. EPA 1985b.)

Black, J.A., W.J. Birge, W.E. McDonnell, A.G. Westerman, B.A. Ramey and D.M. Bruser. 1982. The Aquatic Toxicity of Organic Compounds to Embryo-larval Stages of Fish and Amphibians. Water Resources Research Institute, University of Kentucky, Lexington, Kentucky. Research Rep. No. 133.

Black, J.A., W.J. Birge, A.G. Westerman and P.C. Francis. 1983. Comparative aquatic toxicology of aromatic hydrocarbons. Fundam. Appl. Toxicol. 3: 353-358.

Blackman, G.E., M.H. Parke and F. Garton. 1955. The physiological action of substituted phenols: I. Relationship between chemical structure and physiological activity. Arch. Biochem. Biophys. 54: 45-54.

Bogaruds, R.B. *et al.* 1976. The Avoidance Responses of Selected Wabash River Fishes to Monochloramines. Manuscript. (Cited in Ontario Ministry of the Environment 1979.)

Borgmann, U., O. Kramar and C. Loveridge. 1978. Rates of mortality, growth, and biomass production of *Lymnaea palustris* during chronic exposure to lead. J. Fish. Res. Board Can. 35: 1109-1115.

Borgmann, U., R. Cove and C. Loveridge. 1980. Effect of metals on the biomass production kinetics of freshwater copepods. Can. J. Fish. Aquat. Sci. 37: 567-575.

Boudou, A. and F. Ribeyre. 1984. Influence of exposure length on the direct bioaccumulation of two mercury compounds by *Salmo gairdneri* (fry) and the relationship between organism weight and mercury concentrations. Water Res. 18: 81-86.

Bowling, J.W., G.J. Leversee, P.F. Landrum and J.P. Giesy. 1983. Acute mortality of anthracene-contaminated fish exposed to sunlight. Aquat. Toxicol. 3: 79-80.

Brenniman, G., R. Hartung and W.J. Weber, Jr. 1976. A continuous flow bioassay method to evaluate the effects of outboard motor exhausts and selected aromatic toxicants on fish. Water Res. 10: 165-169.

Brett, J.R. 1956. Some principles in the thermal requirements of fishes. Q. Rev. Biol. 31: 75-87.

Brett, J.R. 1960. Thermal requirements of fish – three decades of study, 1940-1970. *In* Biological Problems in Water Pollution. C.M. Tarzwell (ed.). Public Health Service, U.S. Dep. of Health, Education and Welfare.

Bridges, W.R. 1965. Effects of time and temperature on the toxicity of heptachlor and kepone to redear sunfish. *In* Biological Problems in Water Pollution, 3rd seminar, 1962. C.M. Tarzwell (ed.). U.S. Public Health Service. 999-WP-25. p. 247. (Cited in U.S. EPA 1980ah.)

Bringmann, G. 1975. Determination of biologically harmful effect of water pollutants by means of the retardation of cell proliferation of the blue algae *Microcystis*. Gesund. Ing. 96: 238-241.

Bringmann, G. and R. Kuhn. 1976. Comparative results of the damaging effects of water pollutants against bacteria (*Pseudomonas putida*) and blue algae (*Microcystis aeruginosa*). Gas Wasserfach Wasser Abwasser 117: 410-413.

Bringmann, G. and R. Kuhn. 1977. Limiting values for the damaging action of water pollutants to bacteria (*Pseudomonas putida*) and green alga (*Scenedesmus quadricauda*) in the cell multiplication inhibition test. Z. Wasser Abwasser Forsch. 10: 87-98. (Cited in U.S. EPA 1985g.)

Bringmann, G. and R. Kuhn. 1978a. Testing of substances for their toxicity threshold: model organisms *Microcystis* (*Diplocytis*) *aeruginosa* and *Scenedesmus quadricauda*. Mitt. Int. Ver. Theor. Angew. Limnol. 21: 275-284.

Bringmann, G. and R. Kuhn. 1978b. Limiting values for the noxious effects of water pollutant material to blue algae (*Microcystis aeruginosa*) and green alga (*Scenedesmus quadricauda*) in cell propagation inhibition tests. Vom Wasser 50: 45-60. (Cited in U.S. EPA 1985g.)

Broderius, S.J. and L.L. Smith, Jr. 1979. Lethal and sublethal effects of binary mixtures of cyanide and hexavalent chromium, zinc or ammonia to the fathead minnow (*Pimephales promelas*) and rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 36: 164-172.

Broderius, S.J. and L.L. Smith, Jr. 1980. Direct Photolysis of Hexacyanoferrate Complexes. Proposed Applications to the Aquatic Environment. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-80-003. 50 pp.

Brooks, A.S. and G.L. Seegert. 1977. The Effects of Intermittent Chlorination on the Biota of Lake Michigan. Center for Greater Lakes Studies, University of Wisconsin, Milwaukee, Wisconsin. Spec. Rep. No. 31.

Brown, S.B., J.G. Eales, R.E. Evans and T.J. Hara. 1984. Interrenal, thyroidal, and carbohydrate responses of rainbow trout (*Salmo gairdneri*) to environmental acidification. Can. J. Fish. Aquat. Sci. 41: 36-45.

Brown, V.M. and R.A. Dalton. 1970. The acute lethal toxicity to rainbow trout of mixtures of copper, phenol, zinc and nickel. J. Fish Biol. 2: 211-216.

Brungs, W.A. 1969. Chronic toxicity of zinc to the fathead minnow, *Pimephales promelas* Rafinesque. Trans. Am. Fish. Soc. 98: 272-279.

Brungs, W.A. 1973. Effects of residual chlorine on aquatic life. J. Water Pollut. Control Fed. 45: 2180-2193.

Buccafusco, R.J., S.J. Ells and G.A. LeBlanc. 1981. Acute toxicity of priority pollutants to bluegill (*Lepomis macrochirus*). Bull. Environ. Contam. Toxicol. 26: 446-452.

Buhler, D.R., R.M. Stokes and R.S. Caldwell. 1977. Tissue accumulation and enzymatic effects of hexavalent chromium in rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 34: 9-18.

Burrows, W.D. 1977. Aquatic aluminium: chemistry, toxicology, and environmental prevalence. CRC Crit. Rev. Environ. Control 7: 167-216.

Cairns, J., Jr. 1956. Effects of increased temperatures on aquatic organisms. Ind. Wastes 1: 150-152.

Cairns, J., Jr. and A. Scheier. 1963. Environmental effects upon cyanide toxicity to fish. Not. Natl. Acad. Nat. Sci. Philadelphia 361: 1-11.

Cairns, J., Jr., A.L. Buikema, Jr., A.G. Heath and B.C. Parker. 1978. Effects of Temperature on Aquatic Organism Sensitivity to Selected Chemicals. Bull. 106. Virginia Water Resources Research Center, Blacksburg, Virginia. (Cited in U.S. EPA 1985g.)

Calamari, D., R. Marchetti and G. Vailati. 1977. Effect of prolonged treatments with ammonia on stages of development of *Salmo gairdneri*. Nuovi Ann. Ig. Microbiol. 28: 333-345. (In Italian.)

Calamari, D., R. Marchetti and G. Vailati. 1981. Effects of long-term exposure to ammonia on the developmental stages of rainbow trout (*Salmo gairdneri* Richardson). Rapp. P.V. Reun. Cons. Int. Explor. Mer 178: 81-86.

Calamari, D., G.F. Gaggino and G. Pachetti. 1982. Toxicokinetics of low levels of Cd, Cr, Ni and their mixture in long-term treatment on *Salmo gairdneri* Rich. Chemosphere 11: 59-70.

Calamari, D., S. Galassi, F. Setti and M. Uighi. 1983. Toxicity of selected chlorobenzenes to aquatic organisms. Chemosphere 12: 253-262.

Call, D.J., L.T. Brooke, N. Ahmad and D.D. Vaishnav. 1981. Aquatic Pollutant Hazard Assessments and Development of a Hazard Prediction Technology by Quantitative Structure Activity Relationships. Second Quarterly Report to U.S. EPA Center for Lake Superior Environmental Studies, University of Wisconsin-Superior, Superior, Wisconsin. (Cited in U.S. EPA 1985e.)

Call, D.J., L.T. Brooke, N. Ahmad and J.E. Richter. 1983. Toxicity and Metabolism Studies with EPA Priority Pollutants and Related Chemicals in Freshwater Organisms. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-83-095. (Cited in U.S. EPA 1985b, g.)

Canton, H. and D.M.M. Adema. 1978. Reproducibility of short-term and reproduction toxicity experiments with *Daphnia magna* and comparison of the sensitivity of *Daphnia magna* with *Daphnia pulex* and *Daphnia cucullata* in short-term experiments. Hydrobiologia 59: 135-140.

Cardwell, R.D., D.G. Foreman, T.R. Payne and D.J. Wilbur. 1976a. Acute Toxicity of Selected Toxicants to Six Species of Fish. U.S. Environmental Protection Agency. EPA-600/3-76-008.

Cardwell, R.D., D.G. Foreman, T.R. Payne and D.J. Wilbur. 1976b. Acute toxicity of selenium dioxide to fresh water fishes. Arch. Environ. Contam. Toxicol. 4: 129-144.

Cardwell, R.D., D.G. Foreman, T.R. Payne and D.J. Wilbur. 1977. Acute and Chronic Toxicity of Chlordane to Fish and Invertebrates. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-77-019.

Carlson, R.W. 1984. The influence of pH, dissolved oxygen, suspended solids or dissolved solids upon ventilatory and cough frequencies in the bluegill *Lepomis macrochirus* and brook trout *Salvelinus fontinalis*. Environ. Pollut. 34A: 149-169.

Carroll, J.J., J. Ellis and W.S. Oliver. 1979. Influences of hardness constituents on the acute toxicity of cadmium to brook trout (*Salvelinus fontinalis*). Bull. Environ. Contam. Toxicol. 22: 575-581.

CCREM. 1985. Inventory of Water Quality Guidelines and Objectives 1984. Task Force on Water Quality Guidelines. Canadian Council of Resource and Environment Ministers.

Chakoumakos, C., R.C. Russo and R.V. Thurston. 1979. Toxicity of copper to cutthroat trout (*Salmo clarki*) under different conditions of alkalinity, pH, and hardness. Environ. Sci. Technol. 13: 213-219.

Chapman, G.A. 1975. Toxicity of Copper, Cadmium and Zinc to Pacific Northwest Salmonids. U.S. Environmental Protection Agency, Corvallis, Oregon. (Cited in U.S. EPA 1985c.)

Chapman, G.A. 1978. Effects of continuous zinc exposure on sockeye salmon during adult-to-smolt freshwater residency. Trans. Am. Fish. Soc. 107: 828-836.

Chapman, P.M., M.A. Farrell and R.O. Brinkhurst. 1982a. Relative tolerances of selected aquatic oligochaetes to individual pollutants and environmental factors. Aquat. Toxicol. 2: 47-67. (Cited in Jones 1984.)

Chapman, P.M., M.A. Farrell and R.O. Brinkhurst. 1982b. Relative tolerances of selected aquatic oligochaetes to combinations of pollutants and environmental factors. Aquat. Toxicol. 2: 69-78. (Cited in Jones 1984.)

Chau, Y.K., P.T.S. Wong, B.A. Silverberg, P.L. Luxon and G.A. Bengert. 1976. Methylation of selenium in the aquatic environment. Science 192: 1130-1131.

Christensen, E. and P.A. Zielski. 1980. Toxicity of arsenic and PCB to a green alga (*Chlamydomonas*). Bull. Environ. Contam. Toxicol. 25: 43-48.

Clark, K.L. and D.B. LaZerte. 1985. A laboratory study on the effects of aluminum and pH on amphibian eggs and tadpoles. Can. J. Fish. Aquat. Sci. 42: 1544-1551.

Clark, M.J.R., H. Hanssen, G. van Aggelen and S. Horvath. 1984. Acute toxicity of iron cyanide species to rainbow trout and to *Daphnia magna* under exposure to different light intensities. *In* 11th Annu. Toxicity Workshop. British Columbia Ministry of Environment, Vancouver, British Columbia.

Clemens, H.P. and K.E. Sneed. 1958. Effect of temperature and physiological condition of tolerance of channel catfish to pyridylmercuric acetate (PMA). Prog. Fish Cult. 20: 147-150.

Colgan, P.W., J.A. Cross and P.H. Johansen. 1982. Guppy behavior during exposure to a sub-lethal concentration of phenol. Bull. Environ. Contam. Toxicol. 28: 20-27.

Cope, O.B. 1965. Sport fishery investigation. *In* Effects of Pesticides on Fish and Wildlife, 1964 Research Findings of the Fish and Wildlife Service. U.S. Fish Wildl. Serv. Circ. 226. pp. 51-63.

Coutant, C.C. 1972. Biological aspects of thermal pollution. II. Scientific basis for water temperature standards at power plants. CRC Crit. Rev. Environ. Control 3: 1-24.

Cowgill, U.M. 1973. Biogeochemical cycles for the chemical elements in *Nymphaea odorata* Ait. and the aphid *Rhopalosiphum nymphaeae* (L.) living in Linsley Pond. Sci. Total Environ. 2: 259-303.

CPHA. 1977. Task Force on Arsenic. Final Report. Canadian Public Health Association, Yellowknife, Northwest Territories.

Dalich, G., R. Larson and W. Gingerich. 1982. Acute and chronic toxicity studies with monochlorobenzene in rainbow trout. Aquat. Toxicol. 12: 127-142.

Dauble, D.D., S.A. Barraclough, R.M. Bean and W.E. Fallon. 1983. Chronic effect of coal-liquid dispersions on fathead minnows and rainbow trout. Trans. Am. Fish. Soc. 112: 712-719.

Davies, P.H. and J.P. Goettl. 1975. Study of the Effects of the Metallic Ions on Fish and Aquatic Organisms. Water Pollution Studies N.P. Colorado Dep. Nat. Resourc. Div. Wildl. 7-29.

Davies, P.H. and J.P. Goettl, Jr. 1978. Evaluation of the potential impacts of silver and/or silver iodide on rainbow trout in laboratory and high mountain lake environments. *In* Environmental Impacts of Artificial Ice Nucleating Agents. D.A. Klein (ed.). Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania. p. 149.

Davies, P.H., J.P. Goettl, Jr., J.R. Sinley and N.F. Smith. 1976. Acute and chronic toxicity of lead to rainbow trout *Salmo gairdneri*, in hard and soft water. Water Res. 10: 199-206.

Davis, J.C. 1975. Waterborne Dissolved Oxygen Requirements and Criteria with Particular Emphasis on the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14100. 111 pp.

Davis, J.C. and R.A.W. Hoos. 1975. Use of sodium pentachlorophenate and dehydroabietic acid as reference toxicants for salmonid bioassays. J. Fish. Res. Board Can. 32: 411-416.

De Sylva, D.P. 1969. Theoretical consideration of the effects of heated effluents on marine fishes. *In* Biological Aspects of Thermal Pollution. P.A. Krenkel and F.L. Parker (eds.). Vanderbilt University Press, Nashville, Tennessee. pp. 229-293.

Defoe, D.L., G.D. Veith and R.W. Carlson. 1978. Effects of Aroclor (R) 1248 and 1260 on the fathead minnow (*Pimephales promelas*). J. Fish. Res. Board Can. 35: 997-1002.

DeGraeve, G.M., R.L. Overcast and H.L. Bergman. 1980. Toxicity of underground coal gasification condenser water and selected constituents to aquatic biota. Arch. Environ. Contam. Toxicol. 9: 543-555.

DeGraeve, G.M., R.G. Elder, D.C. Woods and H.L. Bergman. 1982. Effects of naphthalene and benzene on fathead minnows and rainbow trout. Arch. Environ. Contam. Toxicol. 11: 487-490.

Demayo, A. and M.C. Taylor. 1981. Copper. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979a. Arsenic. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979b. Selenium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1980. Lead. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Deshmukh, S.S. and V.B. Marathe. 1980. Size related toxicity of copper and mercury to *Lebistes reticulatus* (Peter), *Labeo rohita* (Ham.) and *Cyprinus carpio* (Linn.). Indian J. Exp. Biol. 18: 421-423.

Devlin, E.W., J.D. Brammer and R.L. Puyear. 1982. Acute toxicity of toluene to three age groups of fathead minnows (*Pimephales promelas*). Bull. Environ. Contam. Toxicol. 29: 12-17.

Dickson, D.R. 1975. Waste Heat in the Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14109. 40 pp.

Dixon, D.G. and J.W. Hilton. 1985. Effects of available dietary carbohydrate and water temperature on the chronic toxicity of waterborne copper to rainbow trout (*Salmo gairdneri*). Can. J. Fish. Aquat. Sci. 42: 1007-1013.

Doudoroff, P. 1976. Toxicity to Fish of Cyanides and Related Compounds: A Review. U.S. Environmental Protection Agency. EPA-600/3-76-038. 154 pp.

Doudoroff, P. 1980. A Critical Review of Recent Literature on Toxicity of Cyanides to Fish. American Petroleum Institute, Washington, D.C. 71 pp.

Doudoroff, P., S.J. Broderius, G. Leduc, G.F. Lee and D.L. Swanson. 1979. Cyanide. *In* A Review of the EPA Red Book: Quality Criteria for Water. R.V. Thurston, R.C. Russo, C.M. Fetterolf, Jr., T.A. Edsall and Y.M. Barber, Jr. (eds.). Water Quality Section, Am. Fish. Soc., Bethesda, Maryland. pp. 106-112.

Dowden, B.F. and H.J. Bennett. 1965. Toxicity of selected chemicals to certain animals. J. Water Pollut. Control Fed. 37: 1308-1316. (Cited in U.S. EPA 1985g.)

Driscoll, C.T., Jr., J.P. Baker, J.J. Bisogni, Jr. and C.L. Schofield. 1980. Effect of aluminium speciation of fish in dilute acidified waters. Nature (London) 284: 161-164.

Eaton, J.G. 1973. Chronic toxicity of a copper, cadmium and zinc mixture to the fathead minnow (*Pimephales promelas* Rafinesque). Water Res. 7: 1723-1736.

Eaton, J.G., J.M. McKim and G.W. Holcombe. 1978. Metal toxicity to embryos and larvae of seven fresh water fish species – 1. Cadmium. Bull. Environ. Contam. Toxicol. 19: 95-103.

EIFAC. 1965. Water quality criteria for European fresh water fish. Report on finely divided solids and inland fisheries. European Inland Fisheries Advisory Commission. Air Water Pollut. 9: 151-168.

EIFAC. 1969. Water quality criteria for European freshwater fish – extreme pH values and inland fisheries. European Inland Fisheries Advisory Commission. Water Res. 3: 593-611.

Environment Canada. 1983a. Hexachlorobutadiene. *In* Guidelines for Surface Water Quality. Vol. 2. Organic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Environment Canada. 1983b. Phthalic acid esters. *In* Guidelines for Surface Water Quality. Vol. 2. Organic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Fandrei, G. and H.L. Collins. 1979. Total residual chlorine: the effect of short-term exposure on the emerald shiner *Notropis atherinoides* (Rafinesque). Bull. Environ. Contam. Toxicol. 23: 262-268. (Cited in U.S. EPA 1985d.)

Federal Water Pollution Control Administration. 1968. Water Quality Criteria. Report of the National Technical Advisory Committee, FWPCA. U.S. Government Printing Office, Washington, D.C. 234 pp.

Ferguson, J.F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6: 1259-1274.

Fetterolf, C.M. 1975. PCB body burdens deny full use of the Great Lakes fishery resource. *In* U.S. EPA Natl. Conf. on Polychlorinated Biphenyls, November 19-21, Chicago, Illinois. pp. 345-347.

Folmar, L.C. 1980. Effects of short-term field applications of acrolein and 2,4-D (DMA) on flavour of the flesh of rainbow trout. Bull. Environ. Contam. Toxicol. 24: 217-224.

Fox, M.E. and S.R. Joshi. 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. J. Great Lakes Res. 10: 190-196.

Franco, P.J., K.L. Daniels, R.M. Cushman and G.A. Kazlow. 1984. Acute toxicity of a synthetic oil, aniline and phenol to laboratory and natural populations of chironomid (Diptera) larvae. Environ. Pollut. 34A: 321-331.

Freeman, H.C. and G.B. Sangalang. 1976. Changes in steroid hormone metabolism as a sensitive method of monitoring pollutants and contaminants. *In* Proc. 3rd Aquatic Toxicity Workshop, Halifax, Nova Scotia. Canada Environmental Protection Service Surv. Rep. EPS-5AR-77-1. (Cited in NRCC 1979a.)

Freeman, R.A. and W.H. Everhart. 1971. Toxicity of aluminium hydroxide complexes in neutral and basic media to rainbow trout. Trans. Am. Fish. Soc. 4: 644-658.

Fromm, P.O. 1980. A review of some physiological and toxicological responses of freshwater fish to acid stress. Environ. Biol. Fishes 5: 79-93.

Fromm, P.O. and R.M. Stokes. 1962. Assimilation and metabolism of chromium by trout. J. Water Pollut. Control Fed. 34: 1151-1155.

Frost, D.V. 1967. Arsenicals in biology – retrospect and prospect. Fed. Proc. Fed. Am. Soc. Exp. Biol. 26: 194-208.

Fry, F.E.J. 1967. Responses of vertebrate poikilotherms to temperature. *In* Thermobiology. A.H. Rose (ed.). Academic Press, New York. pp. 375-409.

Gerhart, E.H. and R.M. Carlson. 1978. Hepatic mixed-function oxidase activity in rainbow trout exposed to several polycyclic aromatic compounds. Environ. Res. 17: 284-295.

Getz, L.L., A.W. Haney, R.W. Larimore, J.A. McNurney, H.V. Leland, P.W. Price, G.L. Rolfe, R.L. Wortman, J.L. Hudson, R.L. Solomon and K.A. Reinbold. 1977. Transport and distribution in a watershed ecosystem. *In* Lead in the Environment. W.R. Boggess and B.G. Wixson (eds.). Prepared for the National Science Foundation, Castle House Publ., Tumbridge Wells, Kent, U.K. NSF/RA-77-214. pp. 105-134.

Geyer, H., G. Politzki and D. Freitag. 1984. Prediction of ecotoxicological behaviour of chemicals: Relationship between n-octanol/water partition coefficient and bioaccumulation of organic chemicals by alga *Chlorella*. Chemosphere 13: 269-284.

Giattina, J.D., R.R. Garton and D.G. Stevens. 1982. Avoidance of copper and nickel by rainbow trout as monitored by a computer-based data acquisition system. Trans. Am. Fish. Soc. 111: 491-504.

Giddings, J.M. 1979. Acute toxicity to *Selenastrum capricornutum* of aromatic compounds from coal conversion. Bull. Environ. Contam. Toxicol. 23: 360-364.

Giesy, J.P., Jr., G.J. Leversee and D.R. Williams. 1977. Effects of naturally occurring aquatic organic fractions on cadmium toxicity to *Simocephalus serrulatus* (Daphnidae) and *Gambusia affinis* (Poeciliidae). Water Res. 11: 1013-1020.

Giles, M.A., H.S. Majewski and B. Hobden. 1984. Osmoregulatory and hematological responses of rainbow trout (*Salmo gairdneri*) to extended environmental acidification. Can. J. Fish. Aquat. Sci. 41: 1686-1694.

Gissel-Nielsen G. and M. Gissel-Nielsen. 1973. Ecological effects of selenium application to field crops. Ambio 2: 114-117.

Gledhill, W.E., R.G. Kaley, W.J. Adams, O. Hicks, P.R. Michael and V.W. Seager. 1980. An environmental safety assessment of butylbenzyl phthalate. Environ. Sci. Technol. 14: 301-305.

Glooschenko, V. and W. Glooschenko. 1975. Effect of polychlorinated biphenyl compounds on growth of Great Lakes phytoplankton. Can. J. Bot. 53: 653-659.

Glooschenko, V. and J.N.A. Lott. 1977. The effects of chlordane on the green alga *Scenedesmus quadricauda* and *Chlamydomonas* sp. Can. J. Bot. 55: 2866-2872.

Goettl, J.P., Jr., P.H. Davies and J.R. Sinley. 1976. Laboratory studies: water pollution studies. *In* Colorado Fisheries Research Review 1972-1975. O.B. Cope (ed.). Colorado Div. Wildl. Publ. DOW-R-R-F72-F75. Denver, Colorado. p. 74.

Grieco, M.P., J.D. Hendricks, R.A. Scanlan, R.O. Sinnhuber and D.A. Pierce. 1978. Carcinogenicity and acute toxicity of dimethylnitrosamine in rainbow trout (*Salmo gairdneri*). J. Natl. Cancer Inst. 60: 1127-1130.

Gunn, J.M. and W. Keller. 1984. Spawning site water chemistry and lake trout (*Salvelinus namaycush*) sac fry survival during spring snowmelt. Can. J. Fish. Aquat. Sci. 41: 319-329.

Gupta, P.K. and P.S. Rao. 1982. Toxicity of phenol, pentachlorophenol and sodium pentachlorophenate to a freshwater pulmonate snail *Lymnaea acuminata* (Lamarck). Arch. Hydrobiol. 94: 210-217.

Hale, J.G. 1977. Toxicity of metal mining wastes. Bull. Environ. Contam. Toxicol. 17: 66-73.

Hallett, D.J. and R.W. Brecher. 1984. Cycling of polynuclear aromatic hydrocarbons in the Great Lakes ecosystem. *In* Toxic Contaminants in the Great Lakes. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, Toronto, Ontario. pp. 213-238.

Halter, M.T., W.J. Adams and H.E. Johnson. 1980. Selenium toxicity to *Daphnia magna*, *Hyallela azteca* and the fathead minnow in hard water. Bull. Environ. Contam. Toxicol. 24: 102-108.

Hamilton, A.L. 1972. A survey of mercury levels in the biota of a mercury-contaminated river system in northwestern Ontario. *In* Mercury in the Aquatic Environment: A Summary of Research Carried Out by the Freshwater Institute, 1970-1971. J.F. Uthe (ed.). Fish. Res. Board Can. Manuscript Rep. Ser. No. 1167. pp. 27-39.

Hart, B.A. 1975. Bioconcentration and toxicity of cadmium in *Chlorella pyrenoidosa*. *In* The Effect of Cadmium on Freshwater Phytoplankton. Prepared for Office of Water Research and Technology, Washington, D.C. PB-257 547. pp. 1-31. (Cited in Reeder *et al*. 1979a).

Hart, B.T. 1974. A Compilation of Australian Water Quality Criteria. Australian Water Resources Council, Department of Environment and Conservation. Australian Government Publ. Serv., Canberra. Tech. Pap. 7. 349 pp.

Harvey, H.H. 1979. The acid deposition problem and emerging research needs in the toxicology of fishes. *In* Proc. 5th Annu. Aquatic Toxicity Workshop, Nov. 1978, Hamilton, Ontario. Can. Fish. Mar. Serv. Tech. Rep. 862. pp. 115-128.

Havas, M. and G.E. Likens. 1985. Toxicity of aluminum and hydrogen ions to *Daphnia catawba*, *Holopedium gibberum*, *Chaoborus punctipennis*, and *Chironomus anthrocinus* from Mirror Lake, New Hampshire. Can. J. Zool. 63: 1114-1119.

Hazel, R.H., C.E. Burkhead and D.G. Huggins. 1979. The Development of Water Quality Criteria for Ammonia and Total Residual Chlorine for the Protection of Aquatic Life in Two Johnson County, Kansas Streams. Office of Water Research and Technology, U.S. Dep. of the Interior, Washington, D.C. 146 pp.

Henderson, D., Q.H. Pickering and C.M. Tarzwell. 1959. Relative toxicity of ten chlorinated hydrocarbon insecticides to four species of fish. Trans. Am. Fish. Soc. 8: 23-32.

Hendrey, G.R., K. Baalsrud, T.S. Traaen, M. Laake and G. Raddum. 1976. Acid precipitation: some hydrobiological changes. Ambio 5: 224-227.

Herbes, S.E. 1976. Transport and bioaccumulation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *In* Coal Technology Program Quarterly Progress Report for the Period Ending December 31, 1975. Oak Ridge National Lab., Oak Ridge, Tennessee. ORNL-5120. pp. 65-70.

Hermanutz, R. 1978. Endrin and malathion toxicity to flagfish (*Jordanella floridae*). Arch. Environ. Contam. Toxicol. 7: 159-168.

Hilton, J.W., P.V. Hodson, H.E. Braun, J.L. Leatherland and S.J. Slinger. 1983. Contaminant accumulation and physiological response in rainbow trout (*Salmo gairdneri*) reared on naturally contaminated diets. Can. J. Fish. Aquat. Sci. 40: 1987-1994.

Hodson, P.V. 1976. δ-amino levulinic acid dehydratase activity of fish blood as an indicator of a harmful exposure to lead. J. Fish. Res. Board Can. 33: 268-271.

Hodson, P.V. and B.R. Blunt. 1981. Temperature-induced changes in pentachlorophenol chronic toxicity to early life stages of rainbow trout. Aquat. Toxicol. 1: 113-127.

Hodson, P.V., D.J. Spry and B.R. Blunt. 1980. Effects on rainbow trout (*Salmo gairdneri*) of a chronic exposure to waterborne selenium. Can. J. Fish. Aquat. Sci. 37: 233-240.

Hodson, P.V., D.M. Whittle and D.J. Hallett. 1984. Selenium contamination of the Great Lakes and its potential effects on aquatic biota. *In* Toxic Contaminants in the Great Lakes. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, Toronto, Ontario. pp. 371-391.

Holcombe, G.W. and R.W. Andrew. 1978. The Acute Toxicity of Zinc to Rainbow and Brook Trout. Comparisons in Hard and Soft Water. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-78-094.

Holcombe, G.W., D.A. Benoit, E.N. Leonard and J.W. McKim. 1976. Long-term effects of lead exposure on three generations of brook trout (*Salvelinus fontinalis*). J. Fish. Res. Board Can. 33: 1731-1734.

Holcombe, G.W., G.L. Phipps and J.T. Fiandt. 1982. Effects of phenol, 2,4-dimethylphenol, 2,4-dichlorophenol, and pentachlorophenol on embryo, larval, and early-juvenile fathead minnows (*Pimephales promelas*). Arch. Environ. Contam. Toxicol. 11: 73-78.

Holcombe, G.W., G.L. Phipps and J.T. Fiandt. 1983. Toxicity of selected priority pollutants to various aquatic organisms. Ecotoxicol. Environ. Saf. 7: 400-409.

Holcombe, G.W., G.L. Phipps, J.L. Knuth and T. Felhaber. 1984. The acute toxicity of selected substituted phenols, nitrobenzenes and benzoic acid esters to fathead minnows *Pimephales promelas*. Environ. Pollut. 35A: 367-381.

Holm, H.W. and M.F. Cox. 1974. Mercury in aquatic systems: Methylation, Oxidation-reduction, and Bioaccumulation. U.S. Environmental Protection Agency, Athens, Georgia. EPA-660/3-74-021.

Holtze, K.E. 1983. Effects of pH and Ionic Strength on Aluminum Toxicity to Early Developmental Stages of Rainbow Trout (*Salmo gairdneri* Richardson). Ontario Ministry of the Environment, Rexdale, Ontario. 39 pp.

Hornshaw, T.C., R.J. Aulerich and H.E. Johnson. 1983. Feeding Great Lakes fish to mink: effects on mink and accumulation and elimination of PCB's by mink. J. Toxicol. Environ. Health 11: 933-946.

Hose, J.E., J.B. Hannah, H.W. Puffer and M.L. Landolt. 1984. Histologic and skeletal abnormalities in benzo(a)pyrene-treated rainbow trout alevins. Arch. Environ. Contam. Toxicol. 13: 675-684.

Houston, A.H. 1982. Thermal Effects Upon Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18566. 200 pp.

Huang, J. and E.F. Gloyna. 1968. Effect of organic compounds on photosynthetic oxygenation – I. Chlorophyll destruction and suppression of photosynthetic oxygen production. Water Res. 2: 347-366.

Huey, D.W. and T.L. Beitinger. 1980. Toxicity of nitrite to larvae of the salamander, *Ambystoma texanum*. Bull. Environ. Contam. Toxicol. 25: 909-912.

Huey, D.A., B.A. Simco and D.W. Criswell. 1980. Nitrite-induced methemoglobin formation in channel catfish. Trans. Am. Fish. Soc. 109: 558-562.

Hutchinson, T.C. 1973. Comparative studies of the toxicity of heavy metals to phytoplankton and their synergistic interaction. Water Pollut. Res. Can. 8: 68-90.

Hutchinson, T.C. and P.M. Stokes. 1975. Heavy metal toxicity and algal bioassays. Water Quality Parameters. American Society for Testing and Materials Spec. Tech. Publ. 573. pp. 320-343.

Hutchinson, T.C., A. Fedorenko, J. Fitchko, A. Kuja, J. VanLoon and J. Lichwa. 1975. Movement and compartmentation of nickel and copper in an aquatic ecosystem. *In* Environmental Biogeochemistry. Vol. 2. J. Nriagu (ed.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 565-585.

IEC Beak Consultants Ltd. 1983. Study of In-mill Effluent Toxicity at the Terrace Bay Pulping Operation. Malton, Ontario. 200 pp. (Cited in Ontario Ministry of the Environment 1984.)

IJC. 1972. Great Lakes Water Quality Agreement of 1972. International Joint Commission, Canada and the United States.

IJC. 1975. Great Lakes Water Quality 1974. 3rd Annual Report. Appendix A. Water Quality Objectives Subcommittee, Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

IJC. 1976. Great Lakes Water Quality 1975. 4th Annual Report. Appendix A. Water Quality Objectives Subcommittee, Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

IJC. 1977. New and Revised Specific Water Quality Objectives. Vol. II. Great Lakes Water Quality Board Report, International Joint Commission, Windsor, Ontario.

IJC. 1978a. Group 2. New and Revised Specific Water Quality Objectives. Proposed for the 1972 Agreement Between the United States and Canada on Great Lakes Water Quality. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

IJC. 1978b. Great Lakes Water Quality Agreement of 1978. International Joint Commission, Canada and the United States.

IJC. 1980. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Advisory Board, International Joint Commission, Windsor, Ontario.

IJC. 1981. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

IJC. 1982. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commisssion, Windsor, Ontario.

IJC. 1983. Annual Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

IJC. 1985. Toxaphene. Draft Report, June. Aquatic Ecosystem Objectives Committee, Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

IJC. 1986. Annual Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

Inglis, A. and E.L. Davis. 1972. Effects of Water Hardness on the Toxicity of Several Organic and Inorganic Herbicides to Fish. U.S. Fish and Wildlife Service, Washington, D.C. Tech. Pap. 67. (Cited in U.S. EPA 1985b.)

Isensee, A.R., P.C. Kearney, E.A. Woolson, G.E. Jones and V.P. Williams. 1973. Distribution of alkyl arsenicals in model ecosystem. Environ. Sci. Technol. 7: 841-845.

Iwama, G.K. and G.L. Greer 1979. Toxicity of sodium pentachlorophenate to juvenile chinook salmon under conditions of high loading density and continuous-flow exposure. Bull. Environ. Contam. Toxicol. 23: 711-716. (Cited in McKee *et al*. 1984.)

Jackson, G.A. 1976. Biologic half-life of endrin in channel catfish tissues. Bull. Environ. Contam. Toxicol. 16: 505-507.

Jarvinen, A.W. and R.M. Tyo. 1978. Toxicity to fathead minnows of endrin in food and water. Arch. Environ. Contam. Toxicol. 7: 409-421.

Jarvinen, A.W., M.J. Hoffman and T.W. Thorslund. 1977. Long-term toxic effects of DDT food and water exposure on fathead minnows (*Pimephales promelas*). J. Fish. Res. Board Can. 34: 2089-2103.

Johnson, W.W. and M.T. Finley. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. Summaries of Toxicity Tests Conducted at Columbia National Fisheries Research Laboratory, 1965-78. Fish and Wildl. Serv., U.S. Dep. of the Interior, Washington, D.C. Res. Publ. 137. 98 pp. (Cited in McKee *et al*. 1984; U.S. EPA 1985b.)

Johnson, W.W. and A.M. Julin. 1980. Acute Toxicity of Toxaphene to Fathead Minnows, Channel Catfish, and Bluegills. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-80-005.

Jones. P.A. 1984. Chlorophenols and Their Impurities in the Canadian Environment: 1983 Supplement. EPS 3-EP-84-3. Commercial Chemicals Branch, Environmental Protection Service, Environment Canada, Ottawa.

Karlander, E.P. and R.W. Krauss. 1972. Absorption and toxicity of beryllium and lithium in *Chlorella vanniellii* Shihira and Krauss. Chesapeake Sci. 13: 245-253. (Cited in U.S. EPA 1980c.)

Kauss, P.B. and T.C. Hutchinson. 1975. Effects of water-soluble petroleum components on the growth of *Chlorella vulgaris* Beijerinck. Environ. Pollut. 9A: 157-174.

Keeney, W.L., W.G. Breck, G.W. VanLoon and J.A. Page. 1976. The determination of trace metals in *Cladophora glomerata – C. glomerata* as a potential biological monitor. Water Res. 10: 981-984.

Kennedy, V.S. and J.S. Mihursky. 1967. Bibliography on the Effects of Temperature in the Aquatic Environment. Natural Resources Institute, University of Maryland, College Park, Maryland. 89 pp.

Kimball, G.L., L.L. Smith, Jr. and S.J. Broderius. 1978. Chronic toxicity of hydrogen cyanide to the bluegill. Trans. Am. Fish. Soc. 197: 341-345.

Kincheloe, J.W., G.A. Wedemeyer and D.L. Koch. 1979. Tolerance of developing salmonid eggs and fry to nitrate exposure. Bull. Environ. Contam. Toxicol. 23: 575-578.

Kinne, O. (ed.). 1970. Marine Ecology. Vol. 1. Environmental Factors. Part I. Wiley Interscience, New York. pp. 321-616.

Knepp, G.L. and G.F. Arkin. 1973. Ammonia toxicity levels and nitrate tolerance of channel catfish. Prog. Fish Cult. 35: 221-224.

Kobayashi, K. and H. Akitake. 1975. Studies on the metabolism of chlorophenols in fish. I. Absorption and excretion of pentachlorophenol by goldfish. Bull. Jpn. Soc. Sci. Fish. 41: 87-92.

Koenst, W.M., L.L. Smith, Jr. and S.J. Broderius. 1977. Effect of chronic exposure of brook trout to sublethal concentrations of hydrogen cyanide. Environ. Sci. Technol. 11: 883-887.

Kovacs, T.G. 1979. The Effect of Temperature on Cyanide Toxicity to Rainbow Trout (*Salmo gairdneri*). I. Acute Effects. II. Chronic Effects. M.Sc. Thesis. Dep. Biol. Sci., Concordia University, Montreal, Quebec.

Kovacs, T.G. and G. Leduc. 1982. Acute toxicity of cyanide to rainbow trout (*Salmo gairdneri*) acclimated at different temperatures. Can. J. Fish. Aquat. Sci. 39: 1426-1429.

Lakota, S., A. Raszka, J. Koszkowski, S. Hlond and F. Kozlowski. 1983. Toxic effects of DDT, lindane, and toxaphene on the fry of the carp, *Cyprinus carpio*, as revealed by an acute test. Folia Biol. (Krakow) 31: 93-99.

Lamb, D.S. and G.C. Bailey. 1981. Acute and chronic effects of alum to midge larvae (Dipteria: Chironomidae). Bull. Environ. Contam. Toxicol. 27: 59-67.

Lamperti, L.P. 1976. Some Effects of Life Stage, Temperature, pH and Alkalinity on the Acute Toxicity of Inorganic Chloramines to Young Coho Salmon (*Oncorhynchus kisutch*). M.S. Thesis. Oregon State University, Corvallis, Oregon. (Cited in U.S. EPA 1985d.)

Langer, O.E. 1980. Effects of sedimentation on salmonid stream life. *In* Report on the Technical Workshop on Suspended Solids and the Aquatic Environment. K. Weagle (ed.). Department of Indian Affairs and Northern Development, Whitehorse, Yukon. Contract No. Ott-80-019. 21 pp.

Larson, G.L., F.E. Hutchins and L.P. Lamperti. 1977. Laboratory determination of acute and sublethal toxicities of inorganic chloramines to early life stages of coho salmon (*Oncorhynchus kisutch*). Trans. Am. Fish. Soc. 106: 268-277.

Larson, G.L., C.E. Warren, F.E. Hutchins, L.P. Lamperti, D.A. Schlesinger and W.K. Seim. 1978. Toxicity of Residual Chlorine Compounds to Aquatic Organisms. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-78-023.

Laseter, J.L., C.K. Bartell, A.L. Laska, D.G. Holmquist and D.B. Condie. 1976. An Ecological Study of Hexachlorobutadiene (HCBD). U.S. Environmental Protection Agency. EPA-68-01-2689.

Laska, A.L., C. Bartell and J. Laseter. 1978. Acute and chronic effects of hexachlorobenzene and hexachlorobutadiene in red swamp crayfish (*Procambarus clarki*) and selected fish species. Toxicol. Appl. Pharmacol. 43: 1-12.

LeBlanc, G.A. 1980. Acute toxicity of priority pollutants to water flea (*Daphnia magna*). Bull. Environ. Contam. Toxicol. 24: 684-691.

LeBlanc, G.A., J.D. Mastone, A.P. Paradice and B.F. Wilson. 1984. The influence of speciation on the toxicity of silver to fathead minnow (*Pimephales promelas*). Environ. Toxicol. Chem. 3: 37-46. (Cited in Jones 1984.)

Leduc, G. 1977. The role of cyanide as an ecological stressing factor to fish. *In* Recent Advances in Fish Toxicology. A Symposium. R.A. Tubb (ed.). U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-77-085. pp. 152-182.

Leduc, G., G. Gravel, L.R. Seguin, B. Vincent and F. Guibert. 1973. The use of sodium cyanide as a fish eradicant in some Quebec lakes. Nat. Can. 100: 1-10.

Leduc, G., R.C. Pierce and I.R. McCracken. 1982. The Effects of Cyanides on Aquatic Organisms with Emphasis upon Fresh Water Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 19246. 139 pp.

Lee, D. 1976. Development of an Invertebrate Bioassay to Screen Petroleum Refinery Effluents Discharged into Fresh Water. Ph.D. Thesis. Virginia Polytechnic Institute and State University, Blackburg, Virginia. (Cited in U.S. EPA 1985g.)

Leino, R.L. and J.H. McCormick. 1984. Morphological and morphometrical changes in chloride cells of the gills of *Pimephales promelas* after chronic exposure to acid water. Cell Tissue Res. 236: 121-128.

Leivestad, H., G. Hendrey, I.P. Muniz and E. Snekvik. 1976. Effects of acid precipitation on freshwater organisms. *In* Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. F.J. Braekke (ed.). S.N.S.F. Project, Norsk Institutt for Skogforskning, Norges Landbrukshogskole, Norway. Research Rep. 6(76). pp. 87-111.

Lemke, A.E. 1980. Comprehensive Report. Interlaboratory Comparison Acute Testing Set. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

Levings, C.D. 1982. The Ecological Consequences of Dredging and Dredge Spoil Disposal in Canadian Waters. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18130. 142 pp.

Lewis, M.A. 1983. Effect of loading density on the acute toxicities of surfactants, copper and phenol to *Daphnia magna* Straus. Arch. Environ. Contam. Toxicol. 12: 51-55.

Lewis, W.M., Jr. and D.P. Morris. 1986. Toxicity of nitrite to fish: a review. Trans. Am. Fish. Soc. 115: 183-195.

Lima, A.R., C. Curtis, D.E. Hammermeister, T.P. Markee, C.E. Northcott and L.T. Brooke. 1984. Acute and chronic toxicities of arsenic(III) to fathead minnows, flagfish, daphnids, and an amphipod. Arch. Environ. Contam. Toxicol. 13: 595-601.

Lind, D.T., L.L. Smith, Jr. and S.J. Broderius. 1977. Chronic effects of hydrogen cyanide on the fathead minnow. J. Water Pollut. Control Fed. 49: 262-268.

Lloyd, D.S. 1985. Turbidity in Fresh Water Habitats of Alaska: A Review of Published and Unpublished Literature Relevant to the Use of Turbidity as a Water Quality Standard. Habitat Division, Alaska Dep. of Fish and Game, Juneau, Alaska. Rep. No. 85-1.

Lock, R.A.C. 1975. Uptake of methylmercury by aquatic organisms from water and food. *In* Sublethal Effects of Toxic Chemicals on Aquatic Animals. Proc. Swedish-Netherlands Symp. J.H. Koeman and J.J.T.W.A. Strik (eds.). Elsevier Sci. Publ. Co., New York. pp. 61-79.

Lock, R.A.C. and A.P. Van Overbeeke. 1981. Effects of mercuric chloride and methylmercuric chloride on mucus secretion in rainbow trout, *Salmo gairdneri* Richardson. Comp. Biochem. Physiol. 69C: 67-73.

Lock, R.A.C., P.M.J.M. Cruijsen and A.P. Van Overbeeke. 1981. Effects of mercuric chloride and methylmercuric chloride on the osmoregulatory function of the gills in rainbow trout, *Salmo gairdneri* Richardson. Comp. Biochem. Physiol. 68C: 151-159.

Lorz, H.W., R.H. Williams and C.A. Fustish. 1978. Effects of Several Metals on Smolting of Coho Salmon. U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-78-090.

Lu, P.-Y. and R.L. Metcalf. 1975. Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. Environ. Health Perspect. 10: 269-284.

Lu, P.-Y., R.L. Metcalf, N. Plummer and D. Mandel. 1977. The environmental fate of three carcinogens; benzo-(a)-pyrene, benzidine, and vinyl chloride evaluated in laboratory model ecosystems. Arch. Environ. Contam. Toxicol. 6: 129-142.

Lunde, G. 1970. Analysis of arsenic and selenium in marine raw materials. J. Sci. Food Agric. 21: 242-247.

Macek, K.J. and W.A. McAllister. 1970. Insecticide susceptibility of some common fish family representatives. Trans. Am. Fish. Soc. 99: 20-27.

Macek, K.J., C. Hutchinson and O.B. Cope. 1969. The effects of temperature on the susceptibility of bluegills and rainbow trout to selected pesticides. Bull. Environ. Contam. Toxicol. 4: 174-183.

Macek, K.J., K.S. Buxton, S.K. Derr, J.W. Dean and S. Sauter. 1976. Chronic Toxicity of Lindane to Selected Aquatic Invertebrates and Fishes. U.S. Environmental Protection Agency, Washington, D.C. EPA 600/3-76-046. (Cited in U.S. EPA 1980aj.)

Macek, K.J., M.A. Lindberg, S. Sauter, K.S. Buxton and P.A. Costa. 1976. Toxicity of Four Pesticides to Water Fleas and Fathead Minnows: Acute and Chronic Toxicity of Acrolein, Heptachlor, Endosulfan, and Trifuluralin to the Water Flea (*Daphnia magna*) and the Fathead Minnow (*Pimephales promelas*). U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-76-099.

MacLeod, J.C. and E. Pessah. 1973. Temperature effects on mercury accumulation, toxicity, and metabolic rate in rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 30: 485-492.

Maki, A.W. and H.E. Johnson. 1975. Effects of PCB (Aroclor (R) 1254) and *p,p'*D T on production and survival of *Daphnia magna* Strauss. Bull. Environ. Contam. Toxicol. 13: 412-416.

Marking, L.L. 1966. Evaluation of *p,p'*-DDT as a reference toxicant in bioassays. *In* Investigations in Fish Control. U.S. Fish Wildl. Serv. Resour. Publ. 14, U.S. Dep. of the Interior. pp. 3-10.

Marking, L.L. 1977. Method of assessing additive toxicity of chemical mixtures. *In* Aquatic Toxicology and Hazard Evaluation. F.L. Mayer and J.L. Hamelink (eds.). American Society for Testing and Materials, Memphis, Tennessee. ASTM Spec. Tech. Publ. 634. pp. 99-108.

Martens, D.W. and J.A. Servizi. 1974. Acute Toxicity of Municipal Sewage to Fingerling Sockeye Salmon. Int. Pacific Salmon Fish. Comm. Prog. Rep. No. 29. New Westminster, British Columbia. 18 pp.

Martens, D.W., R.W. Gordon and J.A. Servizi. 1980. Toxicity of Butoxyethyl Ester of 2,4-D to Selected Salmon and Trout. Int. Pacific Salmon Fish. Comm. Prog. Rep. No. 40. New Westminster, British Columbia.

Mathis, B.J. and T.F. Cummings. 1973. Selected metals in sediments, water and biota in the Illinois River. J. Water Pollut. Control Fed. 45: 1573-1583.

Mattson, V.R., J.W. Arthur and C.T. Walbridge. 1976. Acute Toxicity of Selected Organic Compounds to Fathead Minnows. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-76-097.

Mauck, W.L., P.M. Mehrle and F.L. Mayer. 1978. Effects of the polychlorinated biphenyl Aroclor (R) 1254 on growth, survival, and bone development in brook trout (*Salvelinus fontinalis*). J. Fish. Res. Board Can. 35: 1084-1088.

Mayer, F.L. 1976. Residue dynamics of di-(2-ethylhexyl) phthalate in fathead minnows (*Pimephales promelas*). J. Fish. Res. Board Can. 33: 2610-2613.

Mayer, F.L. and H.O. Sanders. 1973. Toxicology of phthalic acid esters in aquatic organisms. Environ. Health Perspect. 3: 153-157.

Mayer, F.L., P.M. Mehrle, Jr. and W.P. Dwyer. 1975. Toxaphene Effects on Reproduction, Growth and Mortality of Brook Trout. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-75-013.

Mayer, F.L., P.M. Mehrle, Jr. and H.O. Sanders. 1977. Residue dynamics and biological effects of polychlorinated biphenyls in aquatic organisms. Arch. Environ. Contam. Toxicol. 5: 501-511.

Mayer, F.L., P.M. Mehrle, Jr. and W.P. Dwyer. 1977. Toxaphene: Chronic Toxicity to Fathead Minnows and Channel Catfish. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-77-069.

McBride, J.R., H.M. Dye and E.M. Donaldson. 1981. Stress response of juvenile sockeye salmon (*Oncorhynchus nerka*) to the butoxyethanol ester of 2,4-dichlorophenoxyacetic acid. Bull. Environ. Contam. Toxicol. 27: 877-884.

McCarty, L., M. Lupp and M. Shea. 1984. Chlorinated Benzenes in the Aquatic Environment. Scientific Criteria Document for Standard Development No. 3-84. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

McCoy, E.F. 1972. Role of Bacteria in the Nitrogen Cycle in Lakes. U.S. Environmental Protection Agency, Washington, D.C. EPA-16010-EHR-03/72.

McDonald, D.G. 1983. The interaction of environmental calcium and low pH on the physiology of the rainbow trout, *Salmo gairdneri*; I. Branchial and renal net ion and H^+ fluxes. J. Exp. Biol. 102: 123-140.

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. Resources Agency of California State Water Quality Control Board, Sacramento, California. Publ. 3-A.

McKee, P.M., R.P. Scroggins and D.M. Casson. 1984. Chlorinated Phenols in the Aquatic Environment. Scientific Criteria Document for Standard Development No. 2-84. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

McKim, J.M., G.F. Olson, G.W. Holcombe and E.P. Hunt. 1976. Long-term effect of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): toxicity, accumulation, distribution and elimination. J. Fish. Res. Board Can. 33: 2726-2739.

McKim, J.M., J.G. Eaton and G.W. Holcombe. 1978. Metal toxicity to embryos and larvae of eight species of fresh water fish – II. Copper. Bull. Environ. Contam. Toxicol. 19: 608-616.

McLeay, K.J., G.L. Ennis, I.K. Birtwell and G.F. Hartman. 1984. Effects on Arctic Grayling (*Thymallus arcticus*) of Prolonged Exposure to Yukon Placer Mining Sediment: A Laboratory Study. Can. Tech. Rep. Fish. Aquat. Sci. No. 1241. West Vancouver, British Columbia. 96 pp.

McNaught, D.C., D. Griesmer, M. Buzzard and M. Kennedy. 1984. PCB's in Saginaw Bay: Development of Functional Indices to Estimate Inhibition of Ecosystem Fluxes. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-84-008.

Mehrle, P.M. and F.L. Mayer. 1976. Di-2-ethylhexyl phthalate: residue dynamics and biological effects in rainbow trout and fathead minnows. *In* Proc. 10th Annu. Conf. Trace Substances in Environmental Health. D.D. Hemphill (ed.). University of Missouri, Columbia, Missouri. pp. 519-524.

Merkens, J.C. 1958. Studies on the toxicity of chlorine and chloramines to the rainbow trout. Water Waste Treat. J. 7: 150-151. (Cited in U.S. EPA 1985d.)

Messer, J.J., J. Ho and W.J. Grenney. 1984. Ionic strength correction for extent of ammonia ionization in freshwater. Can. J. Fish. Aquat. Sci. 41: 811-815.

Meyn, E.L., R.K. Zajdel and R.V. Thurston. 1984. Acute Toxicity of Ferro Cyanide and Ferric Cyanide to Rainbow Trout. Fish Bioassay Laboratory, Montana State University, Bozeman, Montana. Tech. Rep. 84-1.

Michnowicz, C.J. and T.E. Weaks. 1984. Effects of pH on toxicity of As, Cr, Cu, Ni and Zn to *Selenastrum capricornutum* Printz. Hydrobiologia 118: 299-305.

Miles, J.R.W. and C.R. Harris. 1973. Organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas of Ontario, Canada – 1971. Pestic. Monit. J. 6: 363-368.

Millemann, R.E., W.J. Birge, J.A. Black, R.M. Cushman, K.L. Daniels, P.J. Franco, J.M. Giddings, J.F. McCarthy and A.J. Stewart. 1984. Comparative acute toxicity to aquatic organisms of components of coal-derived synthetic fuels. Trans. Am. Fish. Soc. 113: 74-85.

Moles, A., S. Bates, S.D. Rice and S. Korn. 1981. Reduced growth of coho salmon fry exposed to two petroleum components, toluene and naphthalene in fresh water. Trans. Am. Fish. Soc. 110: 430-436.

Mount, D.I. 1966. The effect of total hardness and pH on acute toxicity of zinc to fish. Air Water Pollut. 10: 49-56.

Mount, D.I. 1969. Developing thermal requirements for freshwater fishes. *In* Biological Aspects of Thermal Pollution. P.A. Krenkel and F.L. Parker (eds.). Vanderbilt University Press, Nashville, Tennessee. pp. 140-147.

Mount, D.I. 1973. Chronic effect of low pH on fathead minnow survival, growth and reproduction. Water Res. 7: 987-993.

Mount, D.I. and T.J. Norberg. 1984. A seven-day life-cycle cladoceran toxicity test. Environ. Toxicol. Chem. 3: 425-434.

Mount, D.M. and C.E. Stephan. 1976. A method of establishing acceptable toxicant limits to fish of malathion and butoxy ethanol ester of 2,4-D. Trans. Am. Fish. Soc. 92: 185-193.

Muir, D.C.G., D.A. Metner, A.P. Blouw, N.P. Grift and W.L. Lockhart. 1980. Effects of water chemistry on the uptake of organic pollutants by fish in river water. *In* Proc. 6th Annu. Aquatic Toxicity Workshop. Can. Tech. Rep. Fish. Aquat. Sci. No. 975. Dep. Fisheries and Oceans, Winnipeg, Manitoba. p. 12.

Murray, C.A. and C.D. Ziebell. 1984. Acclimation of rainbow trout to high pH to prevent stocking mortality in summer. Prog. Fish Cult. 46: 176-179.

Nagy, E., D.S. Painter and B.F. Scott. 1985. Fate and impact of 2,4-D in a pond ecosystem. *In* Proc. 1st Int. Symp. on Watermilfoil (*Myriophyllum spicatum*) and Related Haloragaceae Species, July 23-24, 1985, Vancouver, British Columbia. pp. 202-214.

Namminga, H.E., H.E. Scott and S.L. Burks. 1974. Distribution of copper, load and zinc in selected components of a pond ecosystem. Proc. Okla. Acad. Sci. 54: 62-64.

National Fisheries Research Laboratory. 1980. Unpublished data. Fish and Wildl. Serv., U.S. Dep. of the Interior. (Cited in U.S. EPA 1980b.)

Nebeker, A.V. and F.A. Puglisi. 1974. Effect of polychlorinated biphenyls (PCB's) on survival and reproduction of *Daphnia*, *Gammarus*, and *Tanytarsus*. Trans. Am. Fish. Soc. 103: 722-728.

Nebeker, A.V., F.A. Puglisi and D.L. Defoe. 1974. Effect of polychlorinated biphenyl compounds on survival and reproduction of the fathead minnow and flagfish. Trans. Am. Fish. Soc. 103: 562-568.

Nebeker, A.V., *et al.* 1980. Comparative Sensitivity of Rainbow Trout, Fathead Minnow and *Daphnia magna* to Silver and Endosulfan. Manuscript. (Cited in U.S. EPA 1980ad.)

Nebeker, A.V., J.K. McCrady, R. Mshar and C.K. McAuliffe. 1983. Relative sensitivity of *Daphnia magna*, rainbow trout and fathead minnows to endosulfan. Environ. Toxicol. Chem. 1: 69-72.

Nebeker, A.V., C.K. McAuliffe and R. Mshar. 1983. Toxicity of silver to steelhead and rainbow trout, fathead minnows and *Daphnia magna*. Environ. Toxicol. Chem. 2: 95-104.

Nebeker, A.V., C. Savonen, R.J. Baker and J. McCrady. 1984. Effects of copper, nickel and zinc on the life cycle of the caddisfly *Clistoronia magnifica* (Limnephilidae). Environ. Toxicol. Chem. 3: 645-649.

Nebeker, A.V., C. Savonen and D.G. Stevens. 1985. Sensitivity of rainbow trout early life stages to nickel chloride. Environ. Toxicol. Chem. 4: 233-239.

Nehring, R.B. 1976. Aquatic insects as biological monitors of heavy metal pollution. Bull. Environ. Contam. Toxicol. 15: 147-154.

Neville, C.M. 1985. The physiological response of juvenile rainbow trout, *Salmo gairdneri*, to acid and aluminum – prediction of field responses from laboratory data. Can. J. Fish. Aquat. Sci. 42: 2004-2019.

Nichols, J.W., G.A. Wedemeyer, F.L. Mayer, W.W. Dickhoff, S.V. Gregory, W.T. Yasutake and S.D. Smith. 1984. Effects of fresh water exposure to arsenic trioxide on the parr-smolt transformation of coho salmon (*Oncorhynchus kisutch*). Environ. Toxicol. Chem. 3: 143-149.

Niethammer, K.R., D.H. White, T.S. Baskett and M.W. Sayre. 1984. Presence and biomagnification of organochlorine chemical residues in oxbow lakes of Northeastern Louisiana. Arch. Environ. Contam. Toxicol. 13: 63-74.

Niimi, A.J. and Q.N. LaHam. 1975. Relative toxicity of organic and inorganic compounds of selenium to newly hatched zebrafish (*Brachydanio rerio*). Can. J. Zool. 54: 501-509.

Niimi, A.J. and L. Lowe-Jinde. 1984. Differential blood cell ratios of rainbow trout (*Salmo gairdneri*) exposed to methylmercury and chlorobenzenes. Arch. Environ. Contam. Toxicol. 13: 303-311.

Niimi, A.J. and C.A. McFadden. 1982. Uptake of sodium pentachlorophenate (NaPCP) from water by rainbow trout (*Salmo gairdneri*) exposed to concentrations in the ng/L range. Bull. Environ. Contam. Toxicol. 28: 11-19.

Noggle, C.C. 1978. Behavioral, Physiological and Lethal Effects of Suspended Sediment on Juvenile Salmonids. M.S. Thesis. University of Washington, Seattle, Washington. 87 pp.

NRCC. 1975. Endosulfan: Its Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14098. 100 pp.

NRCC. 1978. Phenoxy Herbicides: Their Effects on Environmental Quality with Accompanying Scientific Criteria for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16075. 440 pp.

NRCC. 1979a. Effects of Cadmium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16743. 148 pp.

NRCC. 1979b. Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. 290 pp.

NRCC. 1981. Effects of Nickel in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18568. 352 pp.

NRCC. 1982. Chlorinated Phenols: Criteria for Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18578. 191 pp.

NRCC. 1983a. 2,4-D: Some Current Issues. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 20647. 99 pp.

NRCC. 1983b. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects on Aquatic Biota. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18981. 209 pp.

Odonnell, A.R., G. Mance and R. Norton. 1984. A Review of the Toxicity of Aluminum in Fresh Water. Water Research Centre, WRC Environment, Medmenham Laboratory, Marlow, Bucks, Great Britain. Tech. Rep. No. TR-197.

Ogata, M. and Y. Miyake. 1973. Identification of substances in petroleum causing objectionable odour in fish. Water Res. 7: 1493-1504.

Olson, G.F., D.I. Mount, V.J. Snarski and T.W. Thorslund. 1975. Mercury residues in fathead minnows, *Pimephales promelas* Rafinesque, chronically exposed to methylmercury in water. Bull. Environ. Contam. Toxicol. 14: 129-134.

Olson, P.A. and R.F. Foster. 1956. Effect of chronic exposure to sodium dichromate of young chinook salmon and rainbow trout. *In* Hanford Biological Research Annual Report for 1955. Hanford Atomic Products Operation, Richland, Washington. HW-41500. pp. 35-47. (Cited in U.S. EPA 1980d.)

Ontario Ministry of the Environment. 1977. St. Clair River Organic Study: Fish Toxicity and Tainting Evaluations for Selected Industrial Effluents. Limnology and Toxicity Section, Water Resources Branch, Toronto, Ontario.

Ontario Ministry of the Environment. 1979. Rationale for the Establishment of Ontario's Provincial Water Quality Objectives. Toronto, Ontario. 236 pp.

Ontario Ministry of the Environment. 1984. Water Management. Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment, Revised. Toronto, Ontario. 70 pp.

Oseid, D. and L.L. Smith, Jr. 1979. The effects of hydrogen cyanide on *Asellus communis* and *Gammarus pseudolimnaeus* and changes in their competitive response when exposed simultaneously. Bull. Environ. Contam. Toxicol. 21: 439-447. (Cited in U.S. EPA 1985g.)

Palachek, R.M. and J.R. Tomasso. 1984. Toxicity of nitrite to channel catfish (*Ictalurus punctatus*), tilapia (*Tilapia aurea*), and largemouth bass (*Micropterus salmoides*): evidence for a nitrite exclusion mechanism. Can. J. Fish. Aquat. Sci. 41: 1739-1744.

Passino, D.R.M. and A.J. Novak. 1984. Toxicity of arsenate and DDT to the cladoceran *Bosmina longirostris*. Bull. Environ. Contam. Toxicol. 33: 325-329.

Patrick, R., T. Bott and R. Larson. 1975. The Role of Trace Elements in Management of Nuisance Growth. U.S. Environmental Protection Agency. EPA-660/2-75-008.

Phipps, G.L., G.W. Holcombe and J.T. Fiandt. 1981. Acute toxicity of phenol and substituted phenols to the fathead minnow. Bull. Environ. Contam. Toxicol. 26: 585-593.

Pickering, Q.H. 1974. Chronic toxicity of nickel to fathead minnow. J. Water Pollut. Control Fed. 46: 760-764.

Pickering, Q.H. 1980. Chronic toxicity of hexavalent chromium to the fathead minnow (*Pimephales promelas*). Arch. Environ. Contam. Toxicol. 9: 405-413.

Pickering, Q.H. and C. Henderson. 1966. Acute toxicity of some important petrochemicals to fish. J. Water Pollut. Control Fed. 38: 1419-1429.

Pickering, Q.H., E.P. Hunt, G.L. Phipps, T.H. Roush, W.E. Smith, D.L. Spehar, E.E. Stephan and D.K. Tanner. 1983. Effects of pollution on fresh water fish and amphibians. J. Water Pollut. Control Fed. 55: 840-863.

Pierce, R.C., S.P. Mathur, D.T. Williams and M.J. Boddington. 1980. Phthalate Esters in the Aquatic Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 17583. 108 pp.

Post, G. and T.R. Schroeder. 1971. Toxicity of four insecticides to four salmonid species. Bull. Environ. Contam. Toxicol. 6: 144-154.

Pruitt, G.W., B.J. Grantham and R.H. Pierce, Jr. 1977. Accumulation and elimination of pentachlorophenol by the bluegill, *Lepomis macrochirus*. Trans. Am. Fish. Soc. 106: 462-465.

Przytocka-Jusiak, M. 1976. Growth and survival of *Chlorella vulgaris* in high concentrations of nitrogen. Acta Microbiol. Pol. 25: 287-289.

Pulp and Paper Research Institute of Canada (PPRIC). 1979. Effects of Pulp Chlorination Conditions on the Formation of Toxic Chlorinated Compounds. Environmental Protection Service, Environment Canada. CPAR Rep. 828-1.

Qureshi, S.A. and A.B. Saksena. 1980. The acute toxicity of some heavy metals to *Tilapia mossambica* (Peters). Aqua (London) 1: 19-20.

Rabe, F.W. and S.B. Bauer. 1977. Heavy metals in lakes of the Coeur d'Alene River Valley, Idaho. Northwest Sci. 51: 183-197.

Ralston, J.G. 1986. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Ramamoorthy, S. and K. Blumhagen. 1984. Uptake of zinc, cadmium, and mercury by fish in the presence of competing compartments. Can. J. Fish. Aquat. Sci. 41: 750-756.

Raney, E.C. and B.W. Menzel. 1967. Heated Effluents and Effects on Aquatic Life with Emphasis on Fishes – a Bibliography. Philadelphia Electric Co. and Ichthyology Bull. No. 1, Philadelphia, Pennsylvania..

Rao, T.S., M. Rao and S.B.S.K. Prasad. 1975. Median tolerance limits of some chemicals to the fresh water fish *Cyprinus carpio*. Indian J. Environ. Health 17: 140-146.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979a. Cadmium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979b. Mercury. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reinbold, K.A. and S.M. Pescitelli. 1982. Effects of Cold Temperature on Toxicity of Ammonia to Rainbow Trout, Bluegills and Fathead Minnows. Project Report. Draft. Contract No. 68-01-5832. Illinois Natural History Survey, Champaign, Illinois.

Reinert, R.E. 1970. Pesticide concentrations in Great Lakes fish. Pestic. Monit. J. 3: 233-240.

Rice, C.P. and M.S. Evans. 1984. Toxaphene in the Great Lakes. *In* Toxic Contaminants in the Great Lakes. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, Toronto, Ontario. pp. 163-194.

Rice, S.D. and J.E. Bailey. 1980. Survival, size and emergence of pink salmon, *Oncorhynchus gorbuscha*, alevins after short- and long-term exposures to ammonia. Fish. Bull. 78: 641-648.

Roberts, J.R., D.W. Rodgers, J.R. Bailey and M.A. Rorke. 1978. Polychlorinated Biphenyls: Biological Criteria for an Assessment of their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16077. 172 pp.

Rodgers, J.H., K.L. Dickson and M.J. DeFoer. 1983. Bioconcentration of lindane and naphthalene in bluegills (*Lepomis macrochirus*). *In* 6th Symp. Aquatic Toxicology and Hazard Assessment. W.E. Bishop, R.D. Cardwell and B.B. Heidolph (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. ASTM Spec. Tech. Publ. 802. pp. 300-311.

Rosner, G., J. Gnittke and C. Kunze. 1979. Influence of phenolics on growth of *Scenedesmus obliquus*. Verh. Ges. Oekol. 8: 383-385.

Ruesink, R.G. and L.L. Smith, Jr. 1975. The relationship of the 96-hour LC_{50} to the lethal threshold concentration of hexavalent chromium, phenol and sodium pentachlorophenate for fathead minnows (*Pimephales promelas* Rafinesque). Trans. Am. Fish. Soc. 104: 567-570.

Russo, R.C. and R.V. Thurston. 1975. Acute Toxicity of Nitrite to Cutthroat Trout (*Salmo clarki*). Fisheries Bioassay Laboratory Tech. Rep. No. 75-3, Montana State University, Bozeman, Montana.

Russo, R.C., C.E. Smith and R.V. Thurston. 1974. Acute toxicity of nitrite to rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 31: 1653-1655.

Saarikoski, J. and M. Viluksela. 1982. Relation between physicochemical properties of phenols and their toxicity and accumulation in fish. Ecotoxicol. Environ. Saf. 6: 501-512. (Cited in Ontario Ministry of the Environment 1984.)

Samecka-Cymerman, A. 1983. The effect of phenol on aquatic mosses *Fontinalis antipyretica* L. and *Platyhypnidium rusciforme* (Neck.) Fleisch in cultures. Pol. Arch. Hydrobiol. 30: 141-147.

Sanborn, J.R., R.L. Metcalf, C.-C. Yu and P.-Y. Lu. 1975. Plasticizers in the environment; the fate of di-*n*-octyl phthalate (DOP) in two model ecosystems and uptake and metabolism of DOP by aquatic organisms. Arch. Environ. Contam. Toxicol. 3: 244-255.

Sanders, H.O. 1969. Toxicology of Pesticides to the Crustacean *Gammarus lacustris*. U.S. Bur. Sport Fish. Wildl. Tech. Pap. 25.

Sanders, H.O. 1972. Toxicity of Some Insecticides to Four Species of Malacostracan Crustaceans. U.S. Bur. Sport Fish. Wildl. Tech. Pap. 66.

Sanders, H.O. 1980. Sublethal Effects of Toxaphene on Daphnids, Scuds and Midges. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-80-006.

Sanders, H.O. and O.B. Cope. 1966. Toxicities of several pesticides to two species of cladocerans. Trans. Am. Fish. Soc. 95: 165-169.

Sanders, H.O. and O.B. Cope. 1968. The relative toxicities of several pesticides to naiads of three species of stoneflies. Limnol. Oceanogr. 13: 112-117.

Sangalang, G.B. and H.C. Freeman. 1979. Tissue uptake of cadmium in brook trout during chronic sublethal exposure. Arch. Environ. Contam. Toxicol. 8: 77-84. (Cited in U.S. EPA 1985c.)

Saskatchewan Ministry of the Environment. 1983. Water Quality Objectives January 1975. 3rd printing. Water Pollution Control Branch, Regina, Saskatchewan.

Sauter, S., K.S. Buxton, K.J. Macek and S.R. Petrocelli. 1976. Effects of Exposure to Heavy Metals on Selected Fresh Water Fish. Toxicity of Copper, Cadmium, Chromium and Lead to Eggs and Fry of Seven Fish Species. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-76-105. (Cited in Reeder *et al.* 1979a.)

Schoettger, R.A. 1970. Toxicology of Thiodan in Several Fish and Aquatic Invertebrates. Investigations in Fish Control 35. U.S. Dep. of the Interior. 31 pp.

Schofield, C.L. 1976. Acid precipitation; effects on fish. Ambio 5: 228-230.

Schofield, C.L. and J.R. Trojnar. 1980. Aluminium toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters. *In* Int. Conf. on Environmental Toxicity, May 21-23, 1979, Rochester, New York. T.Y. Toribara, M.W. Miller and P.E. Morrow (eds.). pp. 341-362. (Cited in Odonnell *et al.* 1984.)

Selby, D.A., J.M. Ihnat and J.J. Messer. 1985. Effects of subacute cadmium exposure on a hardwater mountain stream microcosm. Water Res. 19: 645-655.

Servizi, J.A. and D.W. Martens. 1974. Preliminary Survey of Toxicity of Chlorinated Sewage to Sockey and Pink Salmon. Int. Pacific Salmon Fish. Comm. Prog. Rep. No. 30. New Westminster, British Columbia.

Seydel, I.S. 1972. Distribution and circulation of arsenic through water organisms and sediments of Lake Michigan. Arch. Hydrobiol. 71: 17-30.

Shephard, B. 1983. The Effect of Reduced pH and Elevated Aluminum Concentrations on Three Species of Zooplankton: *Ceriodaphnia reticulata*, *Daphnia magna* and *Daphnia pulex*. U.S. Environmental Protection Agency, Duluth, Minnesota. 14 pp.

Shumway, D.L. and J.R. Palensky. 1973. Impairment of the Flavor of Fish by Water Pollutants. U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-010.

Singleton, H.J. 1985. Water Quality Criteria for Particulate Matter. Resource Quality Section, Water Management Branch, British Columbia Ministry of Environment, Victoria, British Columbia.

Singleton, H.J. 1986. Water Quality Criteria for Cyanide. Resource Quality Section, Water Management Branch, British Columbia Ministry of the Environment, Victoria, British Columbia.

Slonim, A.R. 1973. Acute toxicity of beryllium sulfate to common guppy. J. Water Pollut. Control Fed. 45: 2110-2122.

Slonim, A.R. and E.E. Ray. 1975. Acute toxicity of beryllium sulfate to salamander larvae (*Ambystoma* spp.). Bull. Environ. Contam. Toxicol. 13: 307-312.

Smith, C.E. and W.G. Williams. 1974. Experimental nitrite toxicity in trout and chinook salmon. Trans. Am. Fish. Soc. 103: 389-390.

Smith, E.J., L. Sykora and M.A. Shapiro. 1973. Effect of lime neutralized iron hydroxide suspensions on survival, growth and reproduction of the fathead minnow (*Pimephales promelas*). J. Fish. Res. Board Can. 30: 1147-1153.

Smith, L.L., Jr., S.J. Broderius, D.M. Oseid, G.L. Kimball and W.M. Koenst. 1978. Acute toxicity of hydrogen cyanide to fresh water fishes. Arch. Environ. Contam. Toxicol. 7: 325-337.

Snarski, V.M. and G.F. Olson. 1982. Chronic toxicity and bioaccumulation of mercuric chloride in the fathead minnow (*Pimephales promelas*). Aquat. Toxicol. 2: 143-156.

Snarski, V.M. and F.A. Puglisi. 1976. Effects of Aroclor (R) 1254 on Brook Trout, *Salvelinus fontinalis*. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-76-112.

Snow, J.R. 1958. A preliminary report on the comparative testing of some of the newer herbicides. *In* Proc. 11th Annu. Conf. Southeast. Assoc. Game Fish. Comm., New Orleans, Louisiana. pp. 125-132.

Sodergren, A. 1968. Uptake and accumulation of C^{14}-DDT by *Chlorella* sp. (Chlorophyceae). Oikos 19: 126-138. (Cited in U.S. EPA 1980aa.)

Sodergren, A. 1982. Significance of interfaces in the distribution and metabolism of di-(2-ethylhexyl)phthalate in an aquatic laboratory model ecosystem. Environ. Pollut. 27A: 263-274.

Sorensen, D.L., M.M. McCarthy, E.J. Middlebrooks and D.B. Porcella. 1977. Suspended and Dissolved Solids Effects on Fresh Water Biota: A Review. U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-77-042.

Sorensen, E.M.B. 1976. Thermal effects on the accumulation of arsenic in green sunfish, *Lepomis cyanellus*. Arch. Environ. Contam. Toxicol. 4: 8-17.

Spear, P.A. and R.C. Pierce. 1979. Copper in the Aquatic Environment: Chemistry, Distribution, and Toxicology. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16454. 227 pp.

Spehar, R.L., G.D. Veith, D.L. DeFoe and B.V. Bergstedt. 1979. Toxicity and bioaccumulation of hexachlorocyclopentadiene, hexachloronorbornadiene and heptachloronorborene in larval and early juvenile fathead minnows, *Pimephales promelas*. Bull. Environ. Contam. Toxicol. 21: 576-583.

Speyer, M.R. 1975. Some Effects of Chronic Combined Arsenic and Cyanide Poisoning on the Physiology of Rainbow Trout. M.Sc. Thesis. Dep. Biol. Sci., Concordia University, Montreal, Quebec. 76 pp. (Cited in Leduc *et al*. 1982.)

Sprague, J.B. 1964. Lethal concentrations of copper and zinc for young Atlantic salmon. J. Fish. Res. Board Can. 21: 17-26.

Sprague, J.B. and D.E. Drury. 1969. Avoidance reactions of salmonid fish to representative pollutants J. Fish. Res. Board Can. 26: 169-179.

Stadnyk, L., R.S. Campbell and B.T. Johnson. 1971. Pesticide effect on growth and ^{14}C assimilation in a freshwater alga. Bull. Environ. Contam. Toxicol. 6: 1-8.

Stanley, R.A. 1974. Toxicity of heavy metals and salts to Eurasian water milfoil. Arch. Environ. Contam. Toxicol. 2: 331-341.

Statham, C.N. and J.J. Lech. 1976. Studies on the mechanism of the potentiation of the acute toxicity of 2,4-D *n*-butyl ester and 2′,5-dichloro-4′-nitrosalicylanilide in rainbow trout by carbaryl. Toxicol. Appl. Pharmacol. 36: 281-296.

Stokes, P.M. 1975. Adaptation of green algae to high levels of copper and nickel in aquatic environments. *In* Proc. Int. Conf. on Heavy Metals in the Environment, Toronto, Ontario. Vol. II. Part 1. pp. 137-154.

Stokes, P.M., A.M. Szokalo and J.R. Brown. 1980. Nickel and Copper Uptake by Rainbow Trout (*Salmo gairdneri*) in Acute Toxicity Tests. Unpublished data. (Cited in NRCC 1981.)

Strik, J.J.T.W.A., H.H. deLongh, W.W.A. van Rijn van Alkemade and T.P. Wuite. 1975. Toxicity of chromium (VI) in fish, with special reference to organoweights, liver and plasma enzyme activities, blood parameters and histological alteration. *In* Sublethal Effects of Toxic Chemicals on Aquatic Animals. J.H. Koeman and J.J.T.W.A. Strik (eds.). Elsevier Sci. Publ. Co., New York. pp. 31-41.

Swigert, J.P. and A. Spacie. 1983. Survival and Growth of Warm Water Fishes Exposed to Ammonia Under Low Flow Conditions. Purdue University, West Lafayette, Indiana. 83 pp.

Sykora, J.L., E.J. Smith, M.A. Shapiro and N. Synak. 1972. Chronic effect of ferric hydroxide on certain species of aquatic animals. *In* Proc. 4th Symp. on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pennsylvania. pp. 347-369.

Syracuse Research Corporation. 1983. Health Assessment Document for Toluene. Final Report. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA-608/8-82-008F.

Tarzwell, C.M. and C. Henderson. 1960. Toxicity of less common metals to fishes. Ind. Wastes 5: 12. (Cited in U.S. EPA 1980c.)

Taylor, M.C. 1986. Personal communication. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C. and A. Demayo. 1980. Zinc. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., A. Demayo and S.W. Reeder. 1979. Nickel. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., S.W. Reeder and A. Demayo. 1979. Chromium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., A. Demayo and S.W. Reeder. 1980. Silver. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Thurston, R.V. and E.L. Meyn. 1984. Acute Toxicity of Ammonia to Five Fish Species from the Northwest United States. Fisheries Bioassay Laboratory, Montana State University, Bozeman, Montana. Tech. Rep. 84. 13 pp.

Thurston, R.V. and R.C. Russo. 1983. Acute toxicity of ammonia to rainbow trout. Trans. Am. Fish. Soc. 112: 696-704.

Thurston, R.V., R.C. Russo, C.M. Fetterolf, Jr., T.A. Edsall and Y.M. Barber, Jr. (eds.). 1979. A Review of the EPA Red Book: Quality Criteria for Water. Water Quality Section, Am. Fish. Soc., Bethesda, Maryland. 313 pp.

Thurston, R.V., G.R. Phillips, R.C. Russo and S.M. Hinkins. 1981. Increased toxicity of ammonia to rainbow trout (*Salmo gairdneri*) resulting from reduced concentrations of dissolved oxygen. Can. J. Fish. Aquat. Sci. 38: 983-988.

Thurston, R.V., R.C. Russo and G.A. Vinogradov. 1981. Ammonia toxicity to fishes: effect of pH on the toxicity of the un-ionized ammonia species. Environ. Sci. Technol. 15: 837-840.

Trabalka, J.R. and C.W. Gehrs. 1977. An observation on the toxicity of hexavalent chromium to *Daphnia magna*. Toxicol. Lett. 1: 131-134.

Trujillo, D.A., L.E. Ray, H.E. Murray and S.S. Ciam. 1982. Bioaccumulation of pentachlorophenol by killifish (*Fundulus simitus*). Chemosphere 11: 25-31.

Tsai, C. 1973. Water quality and fish life below sewage outfalls. Trans. Am. Fish. Soc. 102: 281-292. (Cited in U.S. EPA 1985d.)

Tsai, C. and K. Chang. 1981. Effect of sex and size on copper susceptibility of the common guppy, *Lebistes reticulatus* (Peter). J. Fish Biol. 19: 693-689. (Cited in U.S. EPA 1985f.)

Tsai, C. and K. Chang. 1984. Intraspecific variation in copper susceptibility of bluegill sunfish. Arch. Environ. Contam. Toxicol. 13: 93-99. (Cited in U.S. EPA 1985f.)

U.S. EPA. 1973. Water Quality Criteria 1972. Environmental Studies Board, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

U.S. EPA. 1976. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76-023.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency. EPA Contract No. 68-01-4646.

U.S. EPA. 1979. Endosulfan and endosulfan sulfate. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 27-1 to 27-16.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Antimony. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-020.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Arsenic. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-021.

U.S. EPA. 1980c. Ambient Water Quality Criteria for Beryllium. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80024.

U.S. EPA. 1980d. Ambient Water Quality Criteria for Chromium. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-035.

U.S. EPA. 1980e. Ambient Water Quality Criteria for Cyanide. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-037.

U.S. EPA. 1980f. Ambient Water Quality Criteria for Lead. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-057.

U.S. EPA. 1980g. Ambient Water Quality Criteria for Mercury. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-058.

U.S. EPA. 1980h. Ambient Water Quality Criteria for Nickel. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-060.

U.S. EPA. 1980i. Ambient Water Quality Criteria for Nitrosamines. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-064.

U.S. EPA. 1980j. Ambient Water Quality Criteria for Selenium. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-070.

U.S. EPA. 1980k. Ambient Water Quality Criteria for Silver. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-071.

U.S. EPA. 1980l. Ambient Water Quality Criteria for Thallium. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-074.

U.S. EPA. 1980m. Ambient Water Quality Criteria for Zinc. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-079.

U.S. EPA. 1980n. Ambient Water Quality Criteria for Acrolein. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-016.

U.S. EPA. 1980o. Ambient Water Quality Criteria for Aldrin/Dieldrin. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-019.

U.S. EPA. 1980p. Ambient Water Quality Criteria for Benzene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-018.

U.S. EPA. 1980q. Ambient Water Quality Criteria for Chlordane. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-027.

U.S. EPA. 1980r. Ambient Water Quality Criteria for Chlorinated Benzenes. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-028.

U.S. EPA. 1980s. Ambient Water Quality Criteria for Dichlorobenzenes. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-039.

U.S. EPA. 1980t. Ambient Water Quality Criteria for Dichloroethylenes. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-041.

U.S. EPA. 1980u. Ambient Water Quality Criteria for Trichloroethylene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-77.

U.S. EPA. 1980v. Ambient Water Quality Criteria for Tetrachloroethylene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-073.

U.S. EPA. 1980w. Ambient Water Quality Criteria for Chlorinated Phenols. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-032.

U.S. EPA. 1980x. Ambient Water Quality Criteria for Pentachlorophenol. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-065.

U.S. EPA. 1980y. Ambient Water Quality Criteria for 2,4-Dichlorophenol. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-042.

U.S. EPA. 1980z. Ambient Water Quality Criteria for 2-Chlorophenol. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-034.

U.S. EPA. 1980aa. Ambient Water Quality Criteria for DDT. Criteria and Standards Division, U.S. Environmental Protaction Agency, Washington, D.C. EPA-440/5-80-038.

U.S. EPA. 1980ab. Ambient Water Quality Criteria for Dinitrotoluene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-045.

U.S. EPA. 1980ac. Ambient Water Quality Criteria for Diphenylhydrazine. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-062.

U.S. EPA. 1980ad. Ambient Water Quality Criteria for Endosulfan. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-046.

U.S. EPA. 1980ae. Ambient Water Quality Criteria for Endrin. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-047.

U.S. EPA. 1980af. Ambient Water Quality Criteria for Ethylbenzene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-048.

U.S. EPA. 1980ag. Ambient Water Quality Criteria for Haloethers. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-050.

U.S. EPA. 1980ah. Ambient Water Quality Criteria for Heptachlor. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-052.

U.S. EPA. 1980ai. Ambient Water Quality Criteria for Hexachlorobutadiene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-053.

U.S. EPA. 1980aj. Ambient Water Quality Criteria for Hexachlorocyclohexane. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-054.

U.S. EPA. 1980ak. Ambient Water Quality Criteria for Hexachlorocyclopentadiene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-055.

U.S. EPA. 1980al. Ambient Water Quality Criteria for Phenol. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-066.

U.S. EPA. 1980am. Ambient Water Quality Criteria for 2,4-Dimethylphenol. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-044.

U.S. EPA. 1980an. Ambient Water Quality Criteria for Nitrobenzene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-061.

U.S. EPA. 1980ao. Ambient Water Quality Criteria for Nitrophenols. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-063.

U.S. EPA. 1980ap. Ambient Water Quality Criteria for Phthalate Esters. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-067.

U.S. EPA. 1980aq. Ambient Water Quality Criteria for Polychlorinated Biphenyls (PCB's). Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-068.

U.S. EPA. 1980ar. Ambient Water Quality Criteria for Polynuclear Aromatic Hydrocarbons (PAHs). Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-069.

U.S. EPA. 1980as. Ambient Water Quality Criteria for Fluoranthene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-049.

U.S. EPA. 1980at. Ambient Water Quality Criteria for Toluene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-075.

U.S. EPA. 1980au. Ambient Water Quality Criteria for Toxaphene. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-076.

U.S. EPA. 1985a. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1985b. Ambient Water Quality Criteria for Arsenic – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-033.

U.S. EPA. 1985c. Ambient Water Quality Criteria for Cadmium – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-032.

U.S. EPA. 1985d. Ambient Water Quality Criteria for Chlorine – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-030.

U.S. EPA. 1985e. Ambient Water Quality Criteria for Chromium – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-029.

U.S. EPA. 1985f. Ambient Water Quality Criteria for Copper – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-031.

U.S. EPA. 1985g. Ambient Water Quality Criteria for Cyanide – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-028.

U.S. EPA. 1985h. Ambient Water Quality Criteria for Lead – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-027.

U.S. EPA. 1985i. Ambient Water Quality Criteria for Mercury – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-84-026.

U.S. EPA. 1985j. Ambient Water Quality Criteria for Ammonia – 1984. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-85-001.

U.S. EPA. 1986. Ambient Water Quality Criteria for Dissolved Oxygen. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-86-003.

Veith, G.D. and N.M. Austin. 1977. Detection and isolation of bioaccumulable chemicals in complex effluents. *In* Identification and Analysis of Organic Pollutants in Water. L.H. Keith (ed.). Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. pp. 297-302.

Veith, G.D., D.L. DeFoe and B.V. Bergstedt. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Board Can. 36: 1040-1048.

Vocke, R.W., K.L. Sears, J.J. O'Toole and R.B. Wildman. 1980. Growth responses of selected fresh water algae to trace elements and scrubber ash slurry generated by coal-fired power plants. Water Res. 14: 141-150.

Ward, R.W. and G.M. DeGraeve. 1978. Acute residual toxicity of several wastewater disinfectants to aquatic life. Water Resour. Bull. 14: 696-709.

Ward, R.W. and G.M. DeGraeve. 1980. Acute residual toxicity of several disinfectants in domestic and industrial waste water. Water Resour. Bull. 16: 41-48.

Ward, R.W., R.D. Giffin, G.M. DeGraeve and R.A. Stone. 1976. Disinfection Efficiency and Residual Toxicity of Several Wastewater Disinfectants. Vol. 1. Grandville, Michigan. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/2-76-156.

Ward, R.W., R.D. Giffin and G.M. DeGraeve. 1977. Disinfection Efficiency and Residual Toxicity of Several Wastewater Disinfectants. Vol. II. Wyoming, Michigan. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/2-77/203.

Warnick, S.L. and H.L. Bell. 1969. The acute toxicity of some heavy metals to different species of aquatic insects. J. Water Pollut. Control Fed. 4: 280-284.

Watras, C.J., J. MacFarlane and F.M.M. Morel. 1985. Nickel accumulation by *Scenedesmus* and *Daphnia*: food-chain transport and geochemical implications. Can. J. Fish. Aquat. Sci. 42: 724-730.

Webb, P.W. and J.R. Brett. 1973. Effects of sublethal concentrations of sodium pentachlorophenate on growth rate, food conversion efficiency, and swimming performance in underyearling sockeye salmon (*Oncorhynchus nerka*). J. Fish. Res. Board Can. 30: 499-507.

Wedemeyer, G.A. and W.T. Yasatake. 1978. Prevention and treatment of nitrite toxicity in juvenile steelhead trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 35: 822-827. (Cited in Huey and Beitinger 1980.)

West, C.W. 1985. Acute Toxicity of Ammonia to 14 Fresh Water Species. Internal report. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

Westin, D.T. 1974. Nitrate and nitrite toxicity to salmonid fishes. Prog. Fish Cult. 36: 86-89.

WHO. 1984. Guidelines for Drinking-Water Quality. Vol. 1. Recommendations. World Health Organization, Geneva.

Willford, W.A. 1980. Chlorinated hydrocarbons as a limiting factor in the reproduction of lake trout in Lake Michigan. *In* Proc. 3rd USA-USSR Symp. on Effluent Pollution Aquatic Ecosystem. W.R. Swain and V.R. Shannon (eds.). EPA-600/9-80-034. pp. 75-83.

Williamson, D.A. 1983. Surface Water Quality Management Proposal. Vol. 1. Surface Water Quality Objectives. Water Standards and Studies Rep. No. 83-2. Manitoba Dep. of Environment and Workplace Safety and Health, Winnipeg, Manitoba.

Winner, R.W. 1984. Selenium effects on antennal integrity and chronic copper toxicity in *Daphnia pulex* (De Geer). Bull. Environ. Contam. Toxicol. 33: 605-611.

Wobeser, G.A. 1973. Aquatic Mercury Pollution. Studies of its Occurrence and Pathologic Effects on Fish and Mink. Ph.D. Thesis. University of Saskatchewan, Saskatoon, Saskatchewan.

Wolf, E.G., M.J. Schneider, K.O. Schwarzmiller and T.O. Thatcher. 1975. Toxicity Tests on the Combined Effects of Chlorine and Temperature on Rainbow (*Salmo gairdneri*) and Brook (*Salvelinus fontinalis*) Trout. Battelle Pacific Northwest Labs., Richland, Washington. BNWL-SA-5349. 20 pp. (Cited in U.S. EPA 1985d.)

Wong, P.T.S., B.A. Silverberg, Y.K. Chau and P.V. Hodson. 1976. Lead and the Aquatic Biota. Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario.

Wuhrmann, K. and H. Woker. 1955. Influence of temperature and oxygen tension on the toxicity of poisons to fish. Int. Assoc. Theor. Appl. Limnol. 12: 795-801.

Zarafonetis, J.H. and R.E. Hampton. 1974. Some effects of small concentrations of chromium on growth and photosynthesis in algae. Mich. Acad. 6: 417-421.

Zitko, V., W.V. Carson and W.G. Carson. 1975. Thallium: occurrence in the environment and toxicity of fish. Bull. Environ. Contam. Toxicol. 13: 23-30.

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4.0 AGRICULTURAL USES

4.1 IRRIGATION

4.1.1 Introduction

A summary of recommended Canadian water quality guidelines for irrigation is presented in Table 4-1. The following text should be consulted while examining the recommended guidelines in this table.

4.1.1.1 Irrigation in Canada

Canada has about 66 × 10^6 ha of land which is classified as farmland, of which 1% is under irrigation (Table 4-2, Figure 4-1). British Columbia and the Prairie provinces account for 92% (675 000 ha) of the irrigated land in Canada; Alberta supports the largest area of irrigated land (454 000 ha). Ontario and Quebec account for 7.5% (54 700 ha), and the Maritime provinces the remaining 0.5% (1900 ha).

A breakdown of irrigated crops by province was obtained from the census in 1970 (Table 4-3) and more recent data are available for western Canada in Prairie Farm Rehabilitation Administration (Topham 1982). Irrigation of tame hay, forages and some pasture accounted for almost half the irrigated area in Canada (Figure 4-2). About one-fourth of the irrigated land area was sown to cereal crops. The remaining land area was more or less evenly divided among sugar beets, vegetables and fruit trees. Since 1970, there has been a change in irrigated crop patterns, particularly in western Canada. The importance of cereals and forages has increased, with cereals taking the dominant role. The share of irrigated area devoted to potatoes and sugar beets has decreased, while that sown to oilseeds, specialty crops and corn has increased.

The quantity of water used to irrigate crops and the relative importance of different crops can differ markedly from one region of Canada to another. A brief discussion of regional differences in these factors follows.

4.1.1.1.1 British Columbia

The agricultural land in British Columbia is located primarily in mountain valleys, on the interior plateau and on the Fraser River delta. Annual precipitation averages less than 400 mm in the irrigated areas of the Okanagan Basin and in the Kamloops area, and in a small area south of Cranbrook. The Fraser Valley near Vancouver and the east coast of Vancouver Island receive an average of 1600 mm, although most of the precipitation occurs in the nongrowing season. The crop water demand in agricultural areas of British Columbia ranges from 200 to 1200 mm, depending upon the soil texture, crop type and weather conditions (British Columbia Ministry of Agriculture and Food 1983). Near Osoyoos, an orchard or alfalfa crop requires about 1200 mm of irrigation water each year. Farther north near Vernon, rates of 500-750 mm are more representative.

Annual precipitation in the Okanagan Basin, the key area of fruit production in the province, ranges from 380 mm at Vernon in the north to 200 mm at Osoyoos near the U.S. border. Almost 70% of agricultural land in the basin is irrigated. The major irrigated crops north of the Okanagan basin are forages and pastures. In the lower Fraser Valley and Vancouver Island, hay, pasture, vegetables, strawberries, raspberries, cranberries and specialty crops are the mainstay.

Table 4-1. Summary – Guidelines for Irrigation Water Quality

	Guideline ($mg \cdot L^{-1}$)	
Parameter	All soils[1]	Neutral to alkaline soils[2]
Major Ions		
Bicarbonate[3]	—	—
Chloride	100-700 (see Tables 4-4 and 4-5)	—
Sodium	Soils: determine sodium adsorption ratio Crops: see Table 4-6	
Total dissolved solids (salinity)	500-3500 (may not protect some sensitive crops; see Table 4-7)	—
Heavy Metals and Trace Ions[4]		
Aluminum	5.0	20.0
Arsenic	0.1	2.0
Beryllium	0.1	0.5
Boron	0.5-6.0 (see Table 4-8)	—
Cadmium	0.01	—
Chromium	0.1	—
Cobalt	0.05	5.0
Copper	0.2 (Sensitive crops)	5.0
	1.0 (Tolerant crops)	5.0
Fluoride	1.0	15.0
Iron	5.0	20.0
Lead[5]	0.2	2.0
Lithium	2.5	—
Manganese	0.2	10.0
Mercury[3]	—	—
Molybdenum	0.01	0.05
	0.05 (intermittent for acidic soils)	—
Nickel	0.2	2.0
Selenium	0.02	—
	0.05 (intermittent)	—
Uranium[5]	0.01	0.1
Vanadium	0.1	1.0
Zinc	1.0 (soil pH<6.5)	—
	5.0 (soil pH>6.5)	—
Pesticides	Insecticides[3]: — Herbicides: see Table 4-9	
Biological Parameters		
Plant pathogens[3]	—	
Human and animal pathogens[5]	100 fecal coliforms per 100 mL; 1000 total coliforms per 100 mL	

[1] Assumes continuous irrigation unless otherwise noted.

[2] Maximum time of irrigation with water containing elevated concentrations of heavy metals and trace ions is 20 years on neutral to alkaline fine-textured soils.

[3] No guideline recommended at this time.

[4] Guidelines expressed as total concentrations.

[5] Tentative guideline.

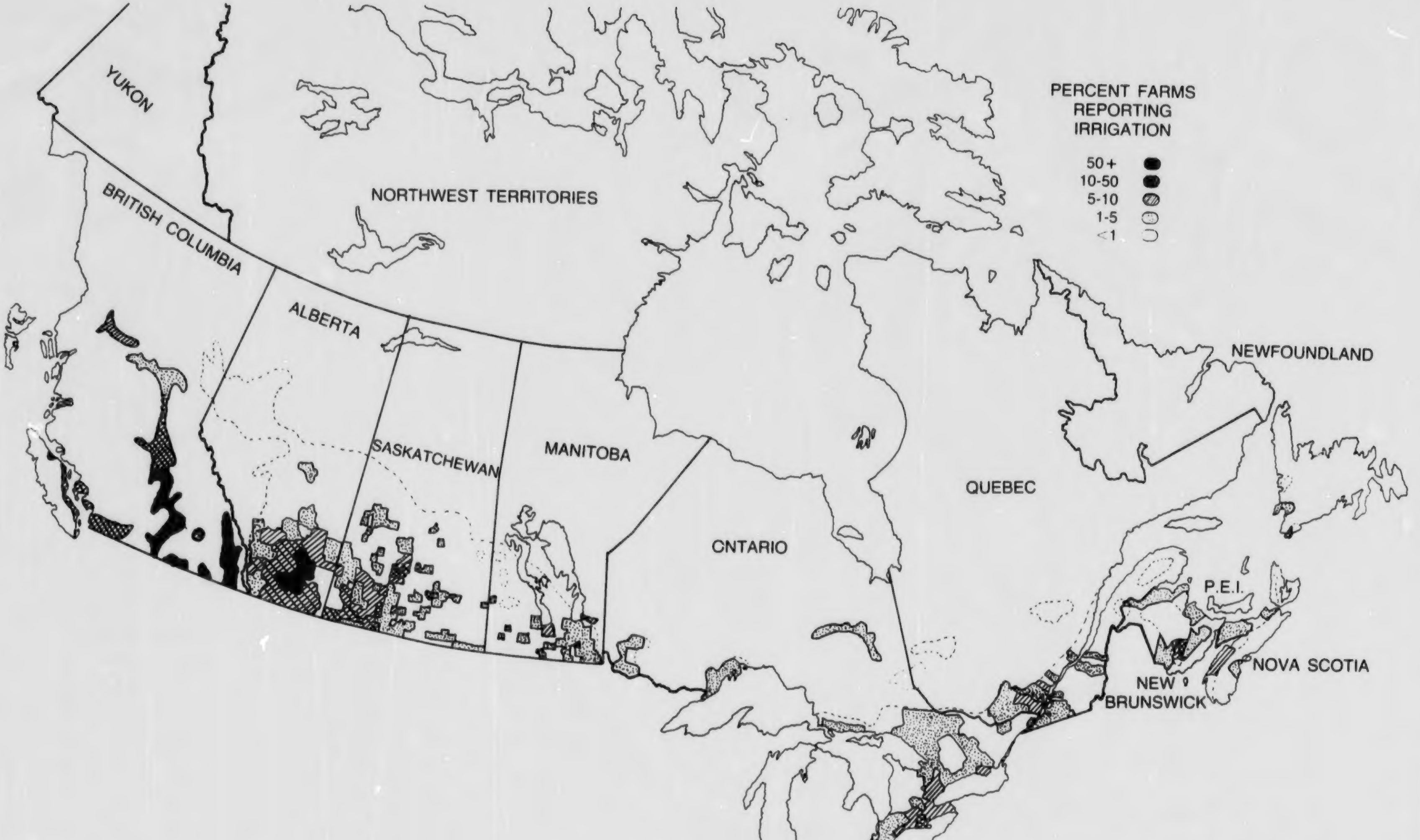
PERCENT FARMS REPORTING IRRIGATION
50+ ●
10-50 ●
5-10 ▨
1-5 ○
<1 ○
YUKON
NORTHWEST TERRITORIES
BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
CNTARIO
QUEBEC
NEWFOUNDLAND
P.E.I.
NOVA SCOTIA
NEW BRUNSWICK

Figure 4-1. Map of Canada showing intensity of irrigation as percentage of farms with irrigation, from 1981 census data (Statistics Canada 1981). The dashed lines delineate land under cultivation (Troughton 1975).

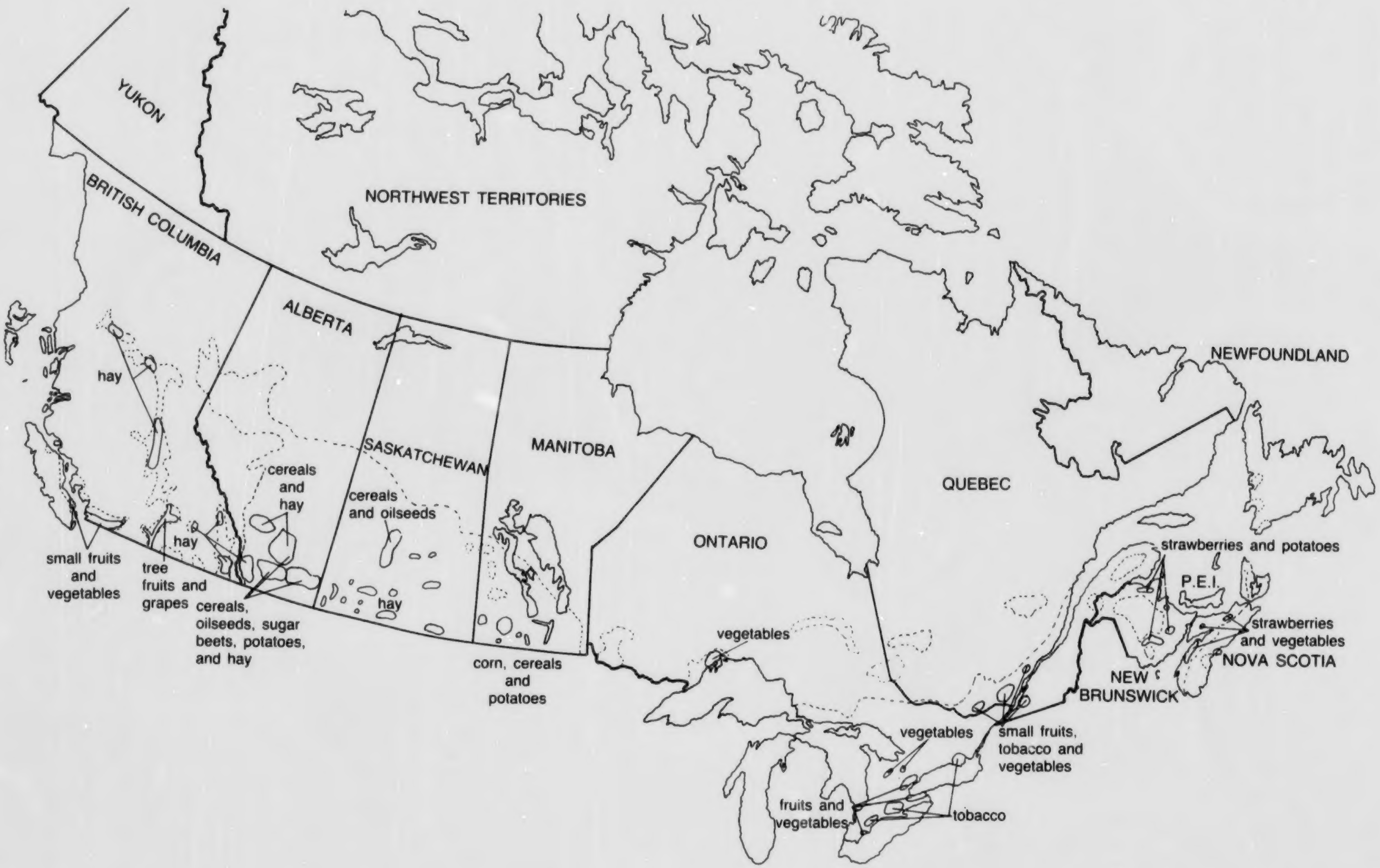
YUKON
BRITISH COLUMBIA
NORTHWEST TERRITORIES
ALBERTA
SASKATCHEWAN
MANITOBA
ONTARIO
QUEBEC
NEWFOUNDLAND
P.E.I.
NEW BRUNSWICK
NOVA SCOTIA
hay
small fruits and vegetables
tree fruits and grapes
hay
cereals, oilseeds, sugar beets, potatoes, and hay
cereals and hay
cereals and oilseeds
hay
corn, cereals and potatoes
vegetables
vegetables
fruits and vegetables
tobacco
small fruits, tobacco and vegetables
strawberries and potatoes
strawberries and vegetables

Figure 4-2. Map of Canada showing approximate location of major irrigated crops in Canada. The dashed lines delineate land under cultivation (Troughton 1975).

4.1.1.1.2 Prairie Provinces

The major irrigated areas within Alberta, Saskatchewan and Manitoba lie within the physiographic region known as the Interior Plains of Canada. Although the Manitoba Lowlands (around Winnipeg) and the Regina Plains represent sections of prairie consisting of flat to gently rolling landscape with little relief, a larger portion of the Prairies consists of a more rolling terrain. This region is occasionally dissected by glacial meltwater channels.

Annual precipitation is 300-400 mm in southwestern Saskatchewan and southeastern Alberta, 400-500 mm in southeastern Saskatchewan and southwestern Manitoba, 500-600 mm in eastern Manitoba, 400 mm along the northern edge of the Prairies and 500-600 mm along the foothills in Alberta (Fisheries and Environment Canada 1978).

Table 4-2. Total Irrigated Farmland for Each of the Provinces of Canada[1]

Province	Total area of farms (ha)	Area under irrigation in 1985 (ha)	Percentage
B.C.	2 178 596	109 000	14.9
Alta.	19 108 513	454 000	62.0
Sask.	25 947 086	101 000	13.8
Man.	7 615 926	11 330	1.5
Ont.	6 039 237	40 000	5.5
P.Q.	3 779 169	14 700	2.0
N.B.	437 888	400	0.1
N.S.	466 023	1 400	0.2
P.E.I.	284 024	80	—
Nfld.	33 454	20	—
	65 888 916	731 930	100

[1] Data for 1985 are estimates obtained by telephone survey from provincial agriculture agencies. The other data are from Statistics Canada (1981).

The annual irrigation requirement for alfalfa in southern Saskatchewan and southern Alberta is 400-500 mm of water (Korven and Randall 1975). Cereal crops and vegetables generally require less irrigation water, but potatoes and sugar beets often require as much as do perennial forage crops.

4.1.1.1.3 Central and Atlantic Canada

In Ontario and Quebec, the major areas of irrigated lands are in the physiographic region of the St. Lawrence Lowlands, which includes southern Ontario and the portion of Quebec adjoining the St. Lawrence River. The Gaspé Peninsula and the Atlantic provinces (New Brunswick, Nova Scotia, Prince Edward Island and Newfoundland) are part of the Appalachian region of Canada.

Average annual precipitation in the drier areas of Ontario is about 800 mm, increasing to 1000 mm over most of Central and Atlantic Canada. In some parts of Nova Scotia, New Brunswick and Newfoundland, annual precipitation averages 1400 mm (Fisheries and Environment Canada 1978). Because of the generally favourable moisture conditions in eastern Canada (>800 mm), irrigation is supplemental. About 100 mm of water per growing season is required. Irrigation is sometimes used as a means of frost protection for strawberries. Adequate drainage is often considered more of a problem than is adequate water supply.

Since the droughts of the early 1950's, Ontario has experienced a considerable growth in irrigation, particularly in the tobacco-growing areas that are situated on coarse-textured soils. The demand for flue-cured tobacco and the value per hectare of this crop, coupled with the incidence of summer moisture deficiencies on the sandy tobacco soils, provided an initial impetus for irrigation development. About two-thirds of the total irrigated area of 40 000 ha is in tobacco. Vegetables

Table 4-3. Percentages of Irrigated Crops in Canada by Province, 1970[1]

Crops	B.C.	Alta.	Sask.	Man.	Ont.	P.Q.	Atlantic prov.	Canada
Tame hay and pasture	65.8	41.8	74.4	16.5	5.6	53.3	19.4	46.6
Cereals	2.7	38.9	16.2	37.0	2.5	21.1	9.5	24.3
Tobacco	—	—	—	—	63.8	7.0	11.5	6.8
Potatoes	1.6	4.2	2.5	14.5	4.4	5.4	30.8	3.9
Sugar beets	—	6.9	—	2.0	—	1.2	—	3.7
Vegetables	4.2	1.2	0.7	21.3	10.8	4.8	13.8	3.2
Tree fruits	14.2	some	some	0.3	3.4	1.2	1.7	3.5
Strawberries	0.5	some	—	1.3	1.8	2.0	10.8	0.5
Other	11.0	7.0	6.2	7.1	7.8	4.0	2.5	7.5
Total irrigated area, 1970 (ha)	89 440	217 660	31 370	2 970	40 256	37 592	2 289	421 577

[1] The statistics for Quebec are an overestimate because the questionnaire from Statistics Canada was interpreted to include both irrigated and drained lands.

Source: Statistics Canada 1971.

and potatoes occupy the next largest area of 6000 ha, followed by some 1500 ha of fruit trees (International Commission on Irrigation and Drainage 1975). Throughout the eastern provinces, irrigation of vegetables, strawberries and fruit trees has helped intensify production while providing a more uniform product and a more reliable supply.

4.1.1.2 Soil Texture

Soil texture plays a major role in irrigation. It determines percolation of water, holding capacity and exchange capacity. Soil texture has been used extensively in irrigation design and scheduling, but has not received the attention it may merit in setting irrigation water quality – soil suitability guidelines.

Most researchers, field advisors and farmers know that poorer quality water used to irrigate sandier soils will sometimes cause problems on heavier soils. Attempts have been made to include texture as part of irrigation water quality guidelines (Schafer 1984). Not only texture, but also the types of clays present can influence soil reaction. Ayers and Wescot (1976) indicated that the sodium permeability problems may be greater in soils with montmorillonite-type clays than in soils with illite-vermiculite clays, and least in kaolinite-sesquioxide clays. This criterion was, however, deleted from their recent guidelines for irrigation with municipal wastewaters (Westcot and Ayers 1984).

It is felt by some researchers that soil texture should be included as a part of the guidelines, particularly in determining combinations of Sodium Adsorption Ratio (SAR) and salinity that afford permeability and salt tolerance protection. It is also a fact, however, that insufficient rationale has been published in the scientific literature to establish texture categories as a standard part of guidelines. Within the next decade(s), texture categorizations and other soil-related categorizations, including depth to impermeable or permeable layers and depth to water tables, will likely form integral parts of water quality – soil suitability guidelines.

At this stage, it would be premature to include textural categorization within national water quality guidelines without an adequate data base and general peer consensus. However, categorization by texture on a provincial level as deemed necessary is desirable.

4.1.1.3 Quality of Water for Irrigation

The suitability of water for irrigation is determined by concentrations of dissolved salts, trace substances and pathogens. The most common problems resulting from use of poor quality water for irrigation are accumulation of salts in the root zone, loss of permeability of soil because of excess sodium or leaching of calcium, and toxicity of ions, trace elements or pesticides. These problems are discussed with the recommended guidelines.

Three important factors should be considered in applying guidelines for irrigation water quality:

1. Quantity of water: Evapotranspiration determines the frequency of irrigation required. In general, the potential for substances from the irrigation water to reach toxic levels in the soil becomes higher as more frequent irrigation is required per year. Precipitation and application of water in excess of crop needs provide protection through leaching of the root zone when drainage is unrestricted.
2. Type of crop: Crops vary widely in their sensitivity to toxic substances.
3. Type of soil: Sandy soils generally have a higher rate of water transmission or percolation than do clay-based soils. Structure and permeability of clay-based soils can be adversely affected by high sodium concentrations.

If the guidelines indicate that water supplies under evaluation may be unsuitable for irrigation, a specialist from the provincial or federal department of agriculture should be consulted to determine how the local conditions of soil type, crop and evapotranspiration rate could modify the effects of water quality.

The guidelines presented here are set to protect the most sensitive crop from toxic concentrations of dissolved ions and other constituents of irrigation water. Unless otherwise stated, they are taken from the Water Quality Criteria 1972, prepared for the United States Environmental Protection Agency (NAS/NAE 1973) as provisional guidelines, to be revised as more data relevant to Canadian climatic conditions and crops become available. The development of these guidelines assumes an annual application rate of irrigation water of 1000 mm, which is typical of California, and retention of trace ions in the surface 15 cm of soil (NAS/NAE 1973). Under these conditions, the recommended maximum concentrations of ions were set to allow irrigation for at least 100 years before thresholds of phytotoxicity would be reached in soils. Higher maximum concentrations were recommended for those ions that are deactivated by neutral and alkaline fine-textured soils for 20 years, after which toxicity to crops might occur if addition of the ions in irrigation water continued. These higher concentrations of ions are applicable to the use of municipal wastewater for irrigation.

Because these guidelines are based on an assumed application rate of 1000 mm of irrigation water per year, which is considerably more than is used in most parts of Canada, the protection provided against buildup of toxic elements in soils should be greater than 100 years.

These guidelines may not protect crops grown in greenhouses without the use of soil (hydroponic method), because many of the recommendations are related to the capacities of soils to deactivate toxic substances.

4.1.2 Major Ions

4.1.2.1 Bicarbonate

4.1.2.1.1 Guideline

No guideline for bicarbonate is recommended at this time.

4.1.2.1.2 Summary of Documents

No recommendations have been made for bicarbonate content of irrigation water in the United States (NAS/NAE 1973) or Australia (Hart 1974), because other soil and water characteristics influence the potential hazard of bicarbonates.

4.1.2.1.3 Rationale

A bicarbonate hazard to soil fertility occurs when irrigation waters containing high concentrations of bicarbonate are used for several decades (Eaton 1950). As the bicarbonate becomes concentrated in the soil water because of evapotranspiration, there is an increased tendency for calcium and magnesium to be precipitated as insoluble carbonates. The result over time is an increased Sodium Adsorption Ratio (SAR) and the manifestation of detrimental effects in the presence of excess sodium.

Several researchers have made attempts to quantify the potential bicarbonate hazard ranging from calculating residual sodium carbonate (RSC) values (Eaton 1950; Wilcox 1958; Bower *et al.* 1968) to calculating adjusted SAR (Rhoades 1968, 1971). Canadian experience has shown that the adjusted SAR is generally 2-3 times the SAR for many waters. It was felt that the adjusted SAR might tend to overcompensate for a potential bicarbonate hazard (Environment Canada 1984; Cameron 1985). The approach of Suarez (1981) for estimating SAR was adopted by Westcot and Ayers (1984), and appears to yield SAR values similar to those from the standard SAR calculation.

4.1.2.2 Chloride

4.1.2.2.1 Guideline

The maximum concentration of chloride in irrigation water should be set according to the sensitivity of a crop to the chloride ion. Sensitive crops should not be irrigated with water containing more than 100 mg·L^{-1} chloride; tolerant crops could be irrigated with water containing as much as 700 mg·L^{-1} chloride (Tables 4-4 and 4-5).

4.1.2.2.2 Summary of Documents

No single maximum concentration of chloride in irrigation water has been recommended in the United States (NAS/NAE 1973) or Australia (Hart 1974), because chloride toxicity varies with type of crop, climatic conditions and method of irrigation. Tolerances of selected crops to chloride were provided in both documents in tabular format. Yield reduction occurs in most crops before other signs of chloride ion toxicity are exhibited (NAS/NAE 1973).

4.1.2.2.3 Rationale

Although chloride is essential to the growth of plants, most woody plant species (stone fruits, citrus, avocados) are sensitive to low concentrations of chloride, whereas most vegetable, grain, forage and fibre crops are not (Chapman 1966; Oster and Rhoades 1984). Chloride damage can occur in two ways. Firstly, the chloride ion can be taken up by the roots and moved upward to accumulate in the leaves, similar to the route taken by sodium. Excessive accumulation causes leaf burn, chlorosis and twig die-back. Secondly, direct foliar absorption of chloride from sprinkler irrigation can cause damage, particularly on hot, windy days (Bernstein 1965).

In Canada, such fruits as apricots, cherries, peaches and plums, and some berry plants, including strawberry, raspberry, boysenberry and blackberry, may be sensitive to root uptake of chloride in irrigation waters ranging in concentrations from 110 to 250 mg·L^{-1} (Table 4-4).

Table 4-4. Chloride Tolerance of Fruit and Woody Crops by Root Uptake

Rootstocks	Cl in irrigation water (mg·L^{-1})	Cultivars	Cl in irrigation water (mg·L^{-1})
Grapes	710-960	Boysenberry Blackberry	250
Stone fruit (peaches, plums, etc.)	180-600	Raspberry	
		Grapes	230-460
		Strawberry	110-180

Source: Westcot and Ayers 1984.

Table 4-5. Sodium or Chloride Concentrations in Irrigation Water Causing Foliar Damage

	Ion concentrations (mg·L^{-1})		
Sensitivity	Cl	Na	Affected crops
Sensitive	<178	<115	Almond, apricot, plum
Moderately sensitive	178-355	115-230	Grape, pepper, potato, tomato
Moderately tolerant	355-710	230-460	Alfalfa, barley, corn, cucumber
Tolerant	>710	>460	Cauliflower, cotton, safflower, sesame, sorghum, sugar beet, sunflower

Source: Westcot and Ayers 1984.

Foliar damage by sprinkler irrigation resulting from excessive absorption of chloride or sodium directly by the leaves is most likely to occur on fruit trees, as they are most sensitive; however, grapes, peppers, potatoes and tomatoes are also sensitive (Table 4-5). Generally, the effects of leaf burn can be minimized by nighttime sprinkling and high application rates, provided that care is taken to prevent erosion.

4.1.2.3 Sodium

4.1.2.3.1 Guideline

Soils can be protected from unfavourable concentrations of sodium if the Sodium Adsorption Ratio (SAR) is calculated and the suitability of irrigation water on a site-by-site basis is determined (Table 4-5).

4.1.2.3.2 Summary of Documents

In their recent guidelines, Westcot and Ayers (1984) categorized the effects of sodium on plants as follows:

SAR (Irrigation Water)	RESTRICTION ON USE
<3	none
3-9	slight to moderate
>9	severe

Table 4-6. Tolerance of Crops to Sodium

Tolerance	SAR of irrigation water	Crop	Conditions
Very sensitive	2-8	Deciduous fruits	Leaf tip burn, leaf scorch
Sensitive	8-18	Beans	Stunted growth
Moderately tolerant	18-46	Clover, oats, tall fescue	Stunted because of nutrition and soil structure
Tolerant	46-102	Wheat, lucerne, barley, tomatoes, beets, tall wheatgrass, crested wheatgrass	Stunted because of soil structure

Source: Hart 1974.

For annual crops which are not sensitive, they suggest a salt tolerance table be used as a guide (Table 4-6).

Detailed discussions of the problems caused by sodium and salinity in irrigation water, and the corrective measures recommended, are available in USDA Handbook 60 (U.S. Department of Agriculture 1954) and Ayers and Westcot (1976, 1985).

4.1.2.3.3 Rationale

Excess sodium in irrigation water relative to calcium and magnesium or relative to the total soluble salt content can adversely affect soil structure and reduce the rate at which water moves into and through the soil (infiltration, permeability), as well as reduce soil aeration. When calcium is the predominant cation of the soil exchange complex, the soil tends to have a granular structure, and be easily workable and permeable. However, when adsorbed sodium exceeds 10-15% of the total cations, the clay becomes dispersed when wetted, which results in a soil that becomes puddled when wet, lowering permeability and forming a hard impermeable crust when dry.

Below the soil surface, permeability can be maintained because an increase in salinity from crop water uptake will usually be sufficient to offset the negative effects of exchangeable sodium.

The magnitude of the effect of excess sodium can be related to the relative proportions of sodium ions and calcium plus magnesium ions in the irrigation water. The Sodium Adsorption Ratio (SAR) can be calculated as follows:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

where concentrations of Na^{+}, Ca^{2+}, and Mg^{2+} are expressed in milliequivalents per litre, as totals.

Most researchers agree that when the SAR approaches 10, the probability of soil permeability problems increases. However, the potential permeability effects of SAR can often be counteracted by high salt concentrations. Quirk and Schofield (1955) and Quirk (1971) showed that there is a clear advantage in increasing the salinity in the irrigation water to maintain soils in a flocculated and permeable condition. Irrigation with water relatively high in sodium and low in total salt may result in poor soil physical conditions; however, waters high in sodium and high in total salt provide stable conditions.

Combinations of salinity (electrical conductivity) and SAR values that lie below the upper curve (Figure 4-3, adapted from Oster and Rhoades 1984) are not expected to cause dispersion or clay swelling, whereas values above the curve can create permeability problems. If the SAR in the topsoil is greater than 10, then large reductions in permeability (puddling, crusting) can occur if rainfall reduces soil salinity to levels below 1 mS·cm^{-1} (Figure 4-3). According to Oster and Rhoades (1984), a 33% loss of soluble salts can be achieved by intermittent ponding of about 4 cm of fresh water on 15 cm of surface soil. In Canadian climates, this factor becomes important, particularly in spring when snowmelt and rain showers can temporarily dilute the surface salt concentration without affecting the percentage of exchangeable sodium in the soil. It is realistic under these situations to provide some degree of protection by extending the zone of potentially unstable conditions, particularly for the more saline waters. Thus, the lower curve in Figure 4-3 is probably more representative of conditions in Canada where irrigation waters with an EC (electrical conductivity) of 1 mS·cm^{-1} and SAR of 6 or less would create stable conditions. Waters with an EC near 3 should not cause permeability problems if the SAR is less than 20. The

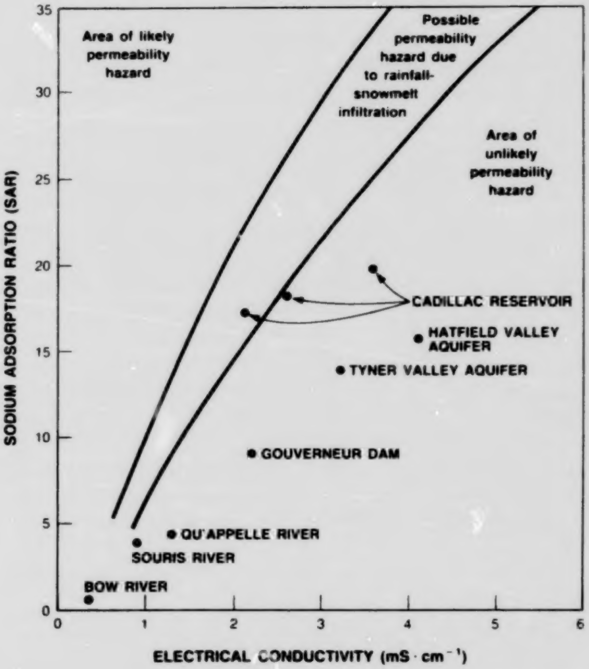

Figure 4-3. **Relationship between salinity and sodium adsorption ratio, showing combinations that promote both favourable and unfavourable conditions for permeability of soil. Upper curve adapted from Oster and Rhoades 1984.**

influence of calcium sulphate in Canadian soils on the dilution of salts by snowmelt and rain showers should be considered.

Sodium can affect plants in five different ways:

1. direct root uptake and plant accumulation of toxic levels of sodium;
2. direct foliar absorption from sprinklers (see Section 4.1.2.3);
3. nutritional imbalance because of insufficient concentrations of calcium and magnesium to prevent the uptake and accumulation of sodium;
4. impairment of soil physical conditions; and
5. sodium is often an important cation contributing to osmotic stress when salinity affects plants.

It is often difficult to separate the various direct and indirect toxic effects of sodium, and usually these are coupled with an overall osmotic or "salinity" effect. Some plants, however, are sodium-sensitive, and can be affected by low concentrations of exchangeable sodium (Table 4-6).

4.1.2.4 Total Dissolved Solids (Salinity)

4.1.2.4.1 Guideline

Generally, if the concentration of total dissolved solids (TDS) in irrigation water does not exceed 1000 $mg \cdot L^{-1}$, a salinity problem would not be expected to occur under normal irrigation practices. At concentrations of 500-1000 $mg \cdot L^{-1}$, some loss in production may be expected for sensitive crops (Table 4-7). In some cases, water containing as much as 3500 $mg \cdot L^{-1}$ of TDS can be used successfully to grow tolerant crops on sandy soils. The suitability of irrigation water containing TDS in the range of 500-3500 $mg \cdot L^{-1}$ should be assessed on a site-by-site basis, considering crop type, soil and internal drainage, with long-term protection of the soil being the goal.

4.1.2.4.2 Summary of Documents

There is a large collection of worldwide literature that deals with the relationship of the salt tolerance of plants to the salinity of irrigation water (Kearney and Scofield 1936; Bernstein 1964, 1965, 1974; Bernstein *et al*. 1972; Ayers and Westcot 1976; Maas and Hoffman 1977; Francois 1981; Westcot and Ayers 1984; Maas 1985). Most of the data have been derived from artificial field plots, where high leaching fractions were maintained to obtain a uniform salt distribution throughout the root zone. Experience has confirmed that such data are reproducible and reliable and have the advantage of being transposed to field situations. Over the years, salt tolerance tables (Table 4-7) showing the relationship between plant sensitivity and irrigation water salinity have been derived from the data.

There have been several concerns about the use of the data in Table 4-7 for Canadian conditions:

1. The crop varieties used to derive the salt tolerances for Table 4-7 are not the same as Canadian varieties, and differences have been observed (McKenzie *et al*. 1983). Canadian wheat and barley varieties do not appear to be as salt-tolerant as those used to derive Table 4-7 and alfalfa might be more salt-tolerant than suggested by Table 4-7.
2. The derivation of the table was based on maximum tolerance without yield reduction of growing (established) plants, but did not account for germination and seedling tolerance. Although barley and wheat are shown as very tolerant crops, actual EC should not exceed 4-5 $mS \cdot cm^{-1}$ during the germination and seedling stages. EC should not exceed 3 $mS \cdot cm^{-1}$ for garden beets and sugar beets during germination.
3. There is concern by researchers that the data in Table 4-7 are more representative of Californian conditions than Canadian conditions. The climate in Canada is cooler and moister, resulting in a greater rate of natural leaching. In addition, the predominant anion in Canadian soils is commonly the sulphate ion, as opposed to the chloride ion in Californian soils.
4. Many of the data have been derived using sandy soil or sand cultures, whereas the irrigated soils in Canada range from sands to clays. Some compensation or adjustment for soil texture should probably be made.

Despite the differences between Canadian crops and growing conditions and those of California, the guidelines of Table 4-7 are routinely applied in Canada with little difficulty, but modifications to suit Canadian agriculture are nonetheless desirable (Jame 1986).

4.1.2.4.3 Rationale

The salinity or total dissolved solids (TDS) concentration of an irrigation water is an extremely important water quality consideration. An increase in salinity causes an increase in the osmotic pressure of the soil solution, resulting in a reduced availability of water for plant consumption.

With adequate drainage, salt accumulation in the soil can be controlled by irrigation management or, more specifically, the rate of application of the water. If the combined application of irrigation and rainfall is lower than plant consumptive use, an accumulation of salts in the main root zone will result. A properly managed irrigation will allow application of sufficient excess water (called leaching fraction) to move a portion of the salts out of the root zone.

Plants vary in their tolerance to salinity of irrigation water. As a general rule, most fruit crops are sensitive, followed by vegetable, field and forage crops (Table 4-7). Within a crop species, there are often varietal differences in salt tolerance. In addition, tolerances vary with different stages of growth; usually the germinating seedling is the most sensitive stage (Millington *et al*. 1951; Hart 1974).

4.1.3 Heavy Metals and Trace Ions

4.1.3.1 Aluminum

4.1.3.1.1 Guideline

The concentration of total aluminum in irrigation water should not exceed 5.0 $mg \cdot L^{-1}$ for continuous use on all soils, or 20 $mg \cdot L^{-1}$ for use up to 20 years on neutral to alkaline fine-textured soils.

Table 4-7. Tolerance of Selected Crops to Total Dissolved Solids in Irrigation Water[1], as Determined by Research in California, U.S.A.

Degree of tolerance	Fruits and berries	Vegetables	Field crops	Forages
Not tolerant				
EC_w <0.7 TDS <500	Strawberry Raspberry	Bean Carrot	Bean	
Slightly tolerant				
EC_w <1.2 TDS <800	Boysenberry Currant Blackberry Gooseberry Plum Grape Apricot Peach Pear Cherry Apple	Onion Parsnip Radish Pea Pumpkin Lettuce Pepper Muskmelon Sweet potato Sweet corn Potato Celery Cabbage Kohlrabi Cauliflower	Cowpea Broadbean Flax Sunflower Corn	Clover (alsike, ladino red and strawberry) Berseem clover Forage corn
Moderately tolerant				
EC_w <2.2 TDS <1500		Spinach Cantaloupe Cucumber Tomato Squash Brussel sprout Broccoli Turnip		Brome, smooth Alfalfa Big trefoil Beardless Wildrye Vetch Timothy Crested wheatgrass
Tolerant				
EC_w <3.6 TDS <2500		Beet Zucchini	Rape Sorghum	Oat hay Wheat hay Brome, mountain Tall fescue Sweet clover Reed Canarygrass Birdsfoot Trefoil Perennial Ryegrass
Very tolerant				
EC_w <5.0 TDS <3500		Asparagus	Soybean Safflower Oats Rye Wheat Sugar beet Barley	Barley hay Tall wheatgrass

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[1] *Assumptions and definitions*:

1. The crops within each "tolerant" grouping are listed from least to most tolerant. Actual tolerances will be modified by management, climate and soil conditions.
2. EC_e means electrical conductivity of saturation extract ($mS \cdot cm^{-1}$ or $mmhos \cdot cm^{-1}$). EC_w is the electrical conductivity of the irrigation water. EC_{sw} is the electrical conductivity of the soil solution. $EC_{sw} = 3EC_w$ for a leaching fraction of 0.15.
3. TDS means total dissolved solids in units of $mg \cdot L^{-1}$. The conversion factor of 1 EC = 700 $mg \cdot L^{-1}$ has been used to transpose data.
4. A leaching fraction of approximately 15% is maintained. The tolerance tables can be adjusted by increasing or decreasing the leaching fraction.
5. Soil texture ranges from sandy loam to clay with good internal drainage and no uncontrolled shallow water table.
6. Rainfall is low and does not play a significant role in meeting crop demands. The guidelines may be too restrictive for wetter areas.
7. Assume the use of gravity and sprinkler irrigation systems where water is applied infrequently as needed. The crop utilizes 50% or more of the stored available water before the next irrigation. Guidelines are too restrictive for frequent or drip irrigation systems.
8. Each irrigation leaches the upper root zone, and salt accumulation increases with depth. The crop responds to the average salinity in the root zone, and the salt content of the soil solution (EC_{sw}) is about three times that of the irrigation water (EC_w) because of evapotranspiration.

Sources: Kearney and Scofield 1936; Bernstein 1964, 1965, 1974; Bernstein *et al.* 1972; Ayers and Westcot 1976; Maas and Hoffman 1977; Francois 1981; Westcot and Ayers 1984; Maas 1985.

4.1.3.1.2 Summary of Documents

The maximum concentration of aluminum recommended for irrigation water on all types of soil is 5.0 mg·L − 1 in both the United States (NAS/NAE 1973) and Australia (Hart 1974); an increase to 20 mg·L − 1 is permitted for 20 years on neutral and alkaline fine-textured soils in the United States. Ontario (Ontario Ministry of the Environment 1984) recommends maximum concentrations of 5.0 and 20.0 mg·L − 1 for waters used continuously on all soils and for use up to 20 years on fine-textured soils of pH 6.0-8.5. Manitoba (Williamson 1983) recommends 5.0 mg·L − 1 for water used as either a sole source or supplemental source of irrigation, and 20.0 mg·L − 1 for use up to 20 years on medium- to fine-textured soils.

4.1.3.1.3 Rationale

Toxicity of aluminum to field crops is an important cause of reduced crop productivity on acid soils, because the solubility of aluminum increases with increasing concentrations of hydrogen ions (Gough *et al.* 1979). Several plants, including wheat and barley, show signs of aluminum toxicity when grown in nutrient solutions that contain between 0.1 and 1 mg·L − 1 aluminum (NAS/NAE 1973). These values cannot be applied directly to irrigation waters because of the capacity of soil to bind and hence reduce the solubility of aluminum ions. These values do, however, indicate that aluminum can be toxic to plants at relatively low concentrations. Because of the general lack of knowledge regarding the concentration of aluminum which would cause toxic response in plants under Canadian conditions, guidelines published for the United States are recommended (NAS/NAE 1973).

4.1.3.2 Arsenic

4.1.3.2.1 Guideline

The concentration of total arsenic in irrigation water should not exceed 0.1 mg·L − 1 for continuous use on all soils and 2.0 mg·L − 1 for use on fine-textured neutral to alkaline soils for up to 20 years. These limits should be reduced if soils have high natural or anthropogenic arsenic content.

4.1.3.2.2 Summary of Documents

The maximum concentrations of arsenic recommended for irrigation water are 0.1 mg·L − 1 for continuous use on all soils and 2.0 mg·L − 1 for use up to 20 years on fine-textured neutral to alkaline soils in the United States (NAS/NAE 1973). The recommended maximum for continuous irrigation in Australia is 0.1 mg·L − 1 (Hart 1984). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommend 0.10 mg·L − 1 for waters used continuously on all soils and 2.0 mg·L − 1 for use up to 20 years on fine-textured soils.

Demayo *et al.* (1979a) recommended maximum concentrations of arsenic according to type of soil and sensitivity of crop: 0.1 mg·L − 1 in sandy loam and 1.0 mg·L − 1 in clay for sensitive crops, and 1.0 mg·L − 1 in sandy loam and 2 mg·L − 1 in clay for tolerant crops. They calculated that a threshold toxic concentration of 5 mg·kg − 1 total arsenic could accumulate from use of water containing 0.1 mg·L − 1 within 10 years in the top 15 cm of soil. However, only a fraction of the total arsenic present in soil is available to plants.

4.1.3.2.3 Rationale

In general, natural levels of arsenic in soils do not exceed 15 mg·kg − 1 (NRCC 1978). Agricultural soils can have elevated concentrations of arsenic because of the past use of organoarsenic pesticides that remain as long-lasting residues (NAS 1977). Agricultural soils in Ontario that were not contaminated with arsenic-based pesticides had concentrations that ranged from 1.1 to 16.7 mg·kg − 1 (Frank *et al.* 1976). Vegetable crops did not grow in soils treated with 500 mg·kg − 1 arsenic (sodium arsenate); crops survived at application rates of 10, 50 and 100 mg·kg − 1, but growth was reduced proportionately (Woolson 1973). The NAS/NAE (1973) summary of the toxic effects of arsenic on plants indicated that reduced growth and toxic symptoms occurred in nutrient solutions containing 0.5-10 mg·L − 1, depending on the plant species. Soils have a high capacity to reduce the toxicity of dissolved arsenic through adsorption to clay and chemical speciation of arsenic as a result of reaction with phosphorus. Direct application of arsenic to soils at 90 kg·ha − 1 generally reduced yield of vegetable crops; at application rates of 45 kg·ha − 1, toxicity to sensitive plants was evident (Jacobs *et al.* 1970). The degree of toxicity of arsenic to plants decreases with increasing clay content in soil (Woolson 1973).

Although root crops such as potatoes and radishes have been shown to concentrate arsenic (Jacobs *et al.* 1970; Woolson 1973), the edible parts of plants do not generally accumulate arsenic to levels dangerous to consumers, because growth is retarded before significant accumulation can occur (NRCC 1978).

4.1.3.3 Beryllium

4.1.3.3.1 Guideline

The concentration of total beryllium in irrigation water should not exceed 0.1 mg·L − 1 for continuous use on all soils and 0.5 mg·L − 1 for use on fine-textured neutral to alkaline soils for up to 20 years.

4.1.3.3.2 Summary of Documents

Maximum concentrations of 0.1 and 0.5 mg·L − 1 beryllium in irrigation water are recommended in the United States for continuous use on all soils and for use on neutral and alkaline soils for up to 20 years (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.3.3 Rationale

In nutrient solution, beryllium was toxic to domestic food and forage plants at concentrations of 0.5-5 mg·L − 1 (NAS/NAE 1973). Growth of cabbage was reduced when beryllium was added to acid soil at a concentration of 40 mg·L − 1, but was not reduced in alkaline soils (Williams and LeRiche 1968). Beryllium is not readily translocated from the roots of plants to foliage, either from nutrient solution or from soil (Gough *et al.* 1979).

4.1.3.4 Boron

4.1.3.4.1 Guideline

The concentration of total boron in irrigation water should not exceed 0.5 mg·L^{-1} for sensitive plants, but could be as high as 6 mg·L^{-1} for tolerant plants (Table 4-8).

4.1.3.4.2 Summary of Documents

The maximum concentrations of boron recommended in the United States (NAS/NAE 1973) and Australia (Hart 1974) for irrigation water on all types of soil are 2 mg·L^{-1} for tolerant crops, 1 mg·L^{-1} for semitolerant crops and 0.3 mg·L^{-1} (Australia) and 0.75 mg·L^{-1} (U.S.A.) for sensitive crops. Up to 2 mg·L^{-1} is permitted for sensitive crops on neutral and alkaline fine-textured soils in the United States for up to 20 years; "higher concentrations" are permitted for tolerant plants or for shorter periods of time. Ontario (Ontario Ministry of the Environment 1984) recommends 0.75 mg·L^{-1} for waters used continuously on all soils and 2.0 mg·L^{-1} for waters used up to 20 years on fine-textured soils of pH 6.0-8.5. Manitoba (Williamson 1983) recommends 0.5 mg·L^{-1} for irrigation water used as a sole source, 1.0 mg·L^{-1} for supplemental irrigation and 2.0 mg·L^{-1} for protection of medium to fine-textured soils up to 20 years.

Table 4-8. Relative Tolerance of Agricultural Crops to Boron

Tolerance[1]	Concentration of boron in soil water[2] (mg·L^{-1})	Agricultural crops
Very sensitive	<0.5	Blackberry
Sensitive	0.5-1.0	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet potato, wheat, barley, sunflower, mung bean, sesame, lupin, strawberry, Jerusalem artichoke, kidney bean, lima bean
Moderately sensitive	1.0-2.0	Red pepper, pea, carrot, radish, potato, cucumber
Moderately tolerant	2.0-4.0	Lettuce, cabbage, celery, turnip, Kentucky bluegrass, oat, corn, artichoke, tobacco, mustard, clover, squash, muskmelon
Tolerant	4.0-6.0	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet, sugar beet
Very tolerant	6.0-15.0	Asparagus

[1] Tolerances will vary with climate, soil conditions and crop varieties; values are to be used only as a guideline.

[2] Maximum concentrations tolerated in irrigation water without reductions in yield or vegetative growth are approximately equal to soil water values or slightly less.

Source: Westcot and Ayers 1984.

4.1.3.4.3 Rationale

Boron is one of the essential elements for plant growth; it is needed in relatively small amounts, and can be toxic when present in excess. Toxic concentrations of boron in irrigation waters are often associated with groundwaters or secondary wastewaters, rather than surface waters (Ayers and Westcot 1976).

A major portion of the boron criteria used for evaluating irrigation waters is based on sand culture work performed in California (Eaton 1944). In a comprehensive review of boron, Gupta *et al.* (1985) concluded that there is confusion in the interpretation of Eaton's data as to whether the "boron concentration" is that of the irrigation water or the soil solution; also, because of the lack of replication in Eaton's work, precision cannot properly be assessed. These authors emphasized the need to establish criteria for evaluating boron in irrigation water. Boron sorption also plays a role in determining soil solution concentrations. Jame *et al.* (1982) developed a theoretical model to aid in predicting boron concentrations in the soil solution.

Concentrations of 1-2 mg·L^{-1} boron can occur in the soil solution only when the adsorptive capacity of the soil is saturated. Thus, sensitive crops can be grown in neutral and alkaline soils without injury from irrigation water containing 2 mg·L^{-1} for a relatively long time (NAS/NAE 1973). Depending on soil type and crop sensitivity, boron may result in some reduced growth, but the net benefit is likely to outweigh avoidance of boron-containing waters in areas where irrigation is necessary. Leaching of boron from soils affords additional protection against buildup to toxic concentrations (Environment Canada 1984).

Despite possible shortcomings of Eaton's data, previous guidelines have been based on them (U.S. Department of Agriculture 1954; Wilcox 1960; Allison 1964; Bingham 1973; NAS/NAE 1973; Bernstein 1974; Hart 1974), and these guidelines have been extensively utilized over the last three decades (Ayers and Westcot 1976; U.S. EPA 1976; Ayers 1977; Shainberg and Oster 1978; Westcot and Ayers 1984; Environment Canada 1984; Maas 1985).

A compilation of the relative tolerance of agricultural crops to boron (Table 4-8) shows that most fruit trees, small fruits and berries are sensitive to boron in soil solution of concentrations in excess of 1.0 mg·L^{-1}. Wheat and barley and such field crops as sunflowers and potatoes are categorized as sensitive, although field crops such as oats, corn, tobacco, mustard, sorghum and sugar beets are tolerant (irrigation water concentrations ranging from 2.0 to 6.0 mg·L^{-1}). Vegetable crops vary in their tolerance: onions and beans are sensitive; peas, carrots, cucumbers, lettuce and celery are moderately affected; and tomatoes, parsley, beets and asparagus are tolerant.

4.1.3.5 Cadmium

4.1.3.5.1 Guideline

The concentration of total cadmium in irrigation water should not exceed 0.01 mg·L^{-1} for continuous use on all soils.

4.1.3.5.2 Summary of Documents

Maximum concentrations of cadmium recommended for irrigation waters in the United States are 0.01 mg·L^{-1} for continuous use on all soils and 0.05 mg·L^{-1} for use to 20 years on neutral and alkaline fine-textured soils (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) also recommends these limits. Manitoba (Williamson 1983) recommends the same limit for cadmium in irrigation water for continuous use on all soils; however, a limit of 0.01 mg·L^{-1} is also recommended for the protection of medium- to fine-textured soils for up to 20 years.

The potential for accumulation in crops used for livestock or human consumption and the known toxicity of the element to both animals and plants (NRCC 1979a) indicate that guidelines for cadmium need to be conservative. Therefore, Reeder *et al.* (1979a) recommended that the maximum concentration of total cadmium in irrigation water used for all Canadian soils not exceed 0.01 mg·L^{-1}. The recommended maximum concentration of cadmium in irrigation waters in Australia is 0.01 mg·L^{-1} (Hart 1984).

4.1.3.5.3 Rationale

Cadmium usually occurs at relatively low concentrations (<0.3 mg·kg^{-1}) in Canadian soils (NRCC 1979a). It is readily taken up by vegetation, although it is not required by plants for metabolism. The rate of cadmium uptake by plants depends on soil type and on levels of other elements, such as copper and zinc. Uptake of cadmium by plants increased with acidity of soil and was inhibited by high levels of clay or organic matter (Friberg *et al.* 1974). Because cadmium is similar to zinc, an essential element for plant growth, it can readily interfere with metabolic processes, and is, therefore, toxic to many plants.

Cadmium in nutrient solutions reduces growth of a diversity of plants, including vegetables and forage species, at levels that range from 0.1 to 1.0 mg·L^{-1} (NAS/NAE 1973). In soils, yield reductions occurred at cadmium levels of 0.11-0.56 mg·L^{-1} in soil solution. Dugdale (1978) cited 50 mg·kg^{-1} of cadmium in soil as the threshold for toxicity to plants, although the first symptoms of cadmium toxicity to wheat (Haghiri 1973) and soybeans (Miller *et al.* 1976) appeared at 2.5 and 1.0 mg·kg^{-1} of soil, respectively. Bingham *et al.* (1975) demonstrated that the yield of a variety of field crops was reduced by 25% at cadmium concentrations that ranged from 4 (spinach) to more than 640 mg·kg^{-1} (rice) in the soil.

4.1.3.6 Chromium

4.1.3.6.1 Guideline

The concentration of total chromium in irrigation water should not exceed 0.1 mg·L^{-1} for continuous use on all soils.

4.1.3.6.2 Summary of Documents

The maximum concentration recommended for chromium in irrigation water in the United States is 0.1 mg·L^{-1} for continuous use on all soils and 1.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommend similar limits. The lower of these values was accepted as applicable to irrigation in Canada by Taylor, Reeder and Demayo (1979), with reference to total chromium. The maximum concentration of total chromium in irrigation water intended for continuous use on all types of soils in Australia is 1.0 mg·L^{-1} (Hart 1984). Future guidelines should probably be written in terms of the more available form, Cr(VI).

4.1.3.6.3 Rationale

Chromium at low concentrations has a beneficial effect on plant growth, and is often included in plant fertilizers, although it is not an essential element for plant growth. Application rates of 10-100 g·ha^{-1} have benefited a diversity of crops (NAS 1974). At relatively high concentrations in controlled environments, chromium can reduce plant productivity.

Chromium at concentrations of 1-10 mg·L^{-1} in nutrient solution reduces plant yield, depending on the variety and species of plant (NAS/NAE 1973; NRCC 1976). When chromium is added to nutrient solution, Cr(III) and Cr(VI) are about equally available to plants (Breeze 1973; Huffman and Allaway 1973). When chromium solution is added to soil, however, Cr(VI) remains mobile and available to plants, whereas Cr(III) is adsorbed or complexed (Breeze 1973). The availability of chromium to plants also depends on the soil and its moisture content. The toxic limits for Cr(VI) range from 5 to 500 mg·kg^{-1} of soil, depending on plant species and soil type (NRCC 1976). Toxic effects of Cr(III) occurred at 50-5000 mg·kg^{-1}.

Over 90% of the chromium absorbed by plants remains in the roots because of poor translocation to aerial parts (Huffman and Allaway 1973). Accumulation of chromium is not known to occur in plants grown for consumption by livestock or people; rather, there is a tendency for foods to contain insufficient chromium (NRCC 1976).

4.1.3.7 Cobalt

4.1.3.7.1 Guideline

The concentration of total cobalt in irrigation water should not exceed 0.05 mg·L^{-1} for continuous use on all soils and 5.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.7.2 Summary of Documents

Recommended maximum concentrations of cobalt in irrigation waters in the United States are 0.05 mg·L^{-1} for continuous use on all soils and 5.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommend these limits also.

4.1.3.7.3 Rationale

Cobalt in nutrient solution has been found to be toxic to a variety of food crops at concentrations of about 0.1-5 mg·L^{-1} (NAS/NAE 1973). There are few studies on the effects of cobalt on crops in which cobalt was applied directly to soils. Vanselow (1966) reported that high concentrations of cobalt

(100 $mg \cdot kg^{-1}$ of soil) had little effect on citrus crops, probably because cobalt is adsorbed by soil particles.

4.1.3.8 Copper

4.1.3.8.1 Guideline

The concentration of total copper in irrigation water should not exceed 0.2 $mg \cdot L^{-1}$ for continuous use on all soils. For irrigation of crops that have a low sensitivity to copper, such as cereals, a maximum copper concentration in irrigation water of 1 $mg \cdot L^{-1}$ is recommended. The concentration of copper may be increased to 5 $mg \cdot L^{-1}$ for use on neutral to alkaline soils for up to 20 years.

4.1.3.8.2 Summary of Documents

The recommended maximum concentrations of copper for irrigation waters in the United States are 0.2 $mg \cdot L^{-1}$ for continuous use on all soils and 5.0 $mg \cdot L^{-1}$ for use up to 20 years on neutral and alkaline fine-textured soils (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommend the same limits. Demayo and Taylor (1981) recommended maximum total copper concentrations in irrigation water of 0.2 $mg \cdot L^{-1}$ for sensitive crops and 1.0 $mg \cdot L^{-1}$ for tolerant crops. Hart (1984) recommended that the maximum total copper concentration in waters used for continuous irrigation be 0.2 $mg \cdot L^{-1}$, regardless of soil type.

4.1.3.8.3 Rationale

Copper is an essential element for plants, and is an important component of several plant enzymes. Symptoms of copper deficiency are common in plants grown in soils low in available copper. For healthy plant growth, the lower limit of copper in soil is about 6 $mg \cdot kg^{-1}$, although higher concentrations of copper are required in organic soils or if concentrations of phosphate, manganese or zinc are high. The natural concentration of copper in soils ranges from about 20 to 50 $mg \cdot kg^{-1}$ (Delas 1963), although certain regions and soils in Canada have much lower amounts of copper. For example, podzolic soils in eastern Canada have less than 20 $mg \cdot kg^{-1}$ copper (Fuller 1977), and agricultural soils in Alberta contain less than 10 $mg \cdot kg^{-1}$ copper (Dudas and Pawluk 1977). Much higher concentrations can occur when soils are exposed to copper from such anthropogenic sources as mining and smelting facilities, continuous irrigation with domestic and industrial sewage, copper-based fungicides, manure produced by animals fed copper-rich diets and some fertilizers.

The first evidence of copper toxicity to copper-sensitive plants occurs at concentrations that range from 25 to 50 $mg \cdot kg^{-1}$ of soil (Delas 1963). However, copper toxicity is usually associated with much higher concentrations, in the order of 150-400 $mg \cdot kg^{-1}$ of soil (Baker 1974). In nutrient solutions, copper toxicity to plants occurs at levels between 0.1 and 17.7 $mg \cdot L^{-1}$, depending on the plant species (NAS/NAE 1973; Demayo and Taylor 1981).

The maximum concentration of 0.2 $mg \cdot L^{-1}$ total copper in irrigation water (Demayo and Taylor 1981) takes into consideration the toxic content of copper in soils for sensitive plants and the accumulation of copper in the top 15 cm of soil, and assumes a soil density of 1700 $kg \cdot m^{-3}$ and an application rate of 1000 mm water per year. At 0.2 $mg \cdot L^{-1}$, 30 years or more would be required before copper would reach concentrations toxic to sensitive plants in soils low in cation-exchange capacity. The time for toxic conditions to develop, 30 years, is underestimated for most of the irrigated regions in Canada, because application rates of 1000 $mm \cdot a^{-1}$ are used only for fruit crops in British Columbia. In other areas of Canada, where irrigation is less frequent, copper concentrations in soil could reach 25 $mg \cdot kg^{-1}$ in, for example, 320 years when water is applied at 100 $mm \cdot a^{-1}$, or in 80 years at 400 mm of water per year.

4.1.3.9 Fluoride

4.1.3.9.1 Guideline

The maximum concentration of total fluoride in irrigation water should not exceed 1.0 $mg \cdot L^{-1}$ for continuous use on all soils, or 15.0 $mg \cdot L^{-1}$ for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.9.2 Summary of Documents

The maximum concentration of fluoride recommended for irrigation water on all types of soil is 1.0 $mg \cdot L^{-1}$ in both the United States (NAS/NAE 1973) and Australia (Hart 1974); an increase to 15.0 $mg \cdot L^{-1}$ is permitted for 20 years on neutral and alkaline fine-textured soils in the United States. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.9.3 Rationale

Concentrations of fluoride in the water of rivers worldwide is in the range of 0.01-0.02 $mg \cdot L^{-1}$; however, industrial wastewaters from the production of aluminum, stainless steel and phosphate fertilizers can contain 8-70 $mg \cdot L^{-1}$ (Rose and Marier 1978). Although much information is available on the effects of gaseous and particulate fluoride on plants, there are few reports of responses of plants to fluoride in the soil (NAS 1971; Rose and Marier 1978).

Genetic damage to the roots of barley (Bale and Hart 1973a, b) and severe damage to the leaves of a horticultural foliage plant, *Cordyline terminalis* (Conover and Poole 1971), resulted when the plants were grown in nutrient solutions containing 0.02 and 0.5 $mg \cdot L^{-1}$ fluoride, respectively. Neutral and alkaline soils have the capacity to deactivate fluoride (NAS/NAE 1973), thereby restricting uptake by roots (Bollard and Butler 1966).

4.1.3.10 Iron

4.1.3.10.1 Guideline

The concentration of total iron in irrigation water should not exceed 5.0 $mg \cdot L^{-1}$ for continuous use on all soils, or 20.0 $mg \cdot L^{-1}$ for use up to 20 years on neutral and alkaline soils.

4.1.3.10.2 Summary of Documents

The recommended maximum concentrations of iron in irrigation water in the United States are 5.0 $mg \cdot L^{-1}$ for continuous use, and 20.0 mg·L^{-1} on neutral and alkaline soils for up to 20 years (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.10.3 Rationale

Plants require iron for growth. Iron deficiency can occur in alkaline soils (Chen and Barak 1982). Dissolved iron in irrigation water precipitates upon aeration; hence it is unavailable to the roots of plants. The precipitate can cause damage to plants by coating the leaves, and may clog irrigation equipment (Hart 1974). Precipitated iron in soil binds the essential elements phosphorus and molybdenum, making them unavailable to plants (NAS/NAE 1973).

4.1.3.11 Lead

4.1.3.11.1 Guideline (Tentative)

The concentration of total lead in irrigation water should not exceed 0.2 mg·L^{-1} for continuous use on all soils, and 2.0 mg·L^{-1} for use on neutral and alkaline fine-textured soils for up to 20 years.

4.1.3.11.2 Summary of Documents

A maximum concentration of lead in irrigation waters of 5.0 mg·L^{-1} was recommended in the United States (NAS/NAE 1973) and in Australia (Hart 1984); a maximum of 10.0 mg·L^{-1} for application over 20 years to neutral and alkaline fine-textured soils was also recommended for the United States. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.11.3 Rationale

The uptake of lead by plants is facilitated by lower pH and low organic content of soils (Jorgensen 1976). Regardless of soil conditions, lead is not readily absorbed through the roots of plants, evidently because of binding to soil. Concentrations of lead tend to be higher in the roots of plants than in the aerial parts, suggesting that translocation does not readily occur (Motto *et al.* 1970; Walsh *et al.* 1976). Perennial ryegrass grown in soils containing 20-149 mg·kg^{-1} total lead accumulated 10-38 mg·kg^{-1} in the roots and 5-7 mg·kg^{-1} in the shoots (Jones and Clement 1972). Soil containing lead at 17 mg·kg^{-1} (dry weight) resulted in the following lead residues in edible plant parts: 0.16 mg·kg^{-1} in wheat; 0.27 mg·kg^{-1} in corn; 0.33 mg·kg^{-1} in potatoes; 0.72 mg·kg^{-1} in tomatoes; 1.1 mg·kg^{-1} in cabbage; 1.2 mg·kg^{-1} in beans; 2.1 mg·kg^{-1} in carrots; and 3.2 mg·kg^{-1} in lettuce (Ter Haar 1970). Plants are capable of accumulating lead residues at concentrations that are potentially hazardous to human consumers and livestock, as was reported for potatoes, lettuce and hay grown in areas contaminated by industrial wastes (Hernberg and Nordman 1972; Hemphill *et al.* 1973).

The presence of lead residues in soil has caused reduced yield of lettuce, but not of oats, at 1000 mg·kg^{-1} (John and Van Laerhoven 1972); poor growth and discolouration of beans, but not of peanuts, at 820 mg·kg^{-1} (Berg 1970); and reduced growth of corn at 125 mg·kg^{-1} (Walker *et al.* 1977). In general, lead is considered to be relatively low in toxicity to plants (NAS/NAE 1973).

If irrigation water containing 5 mg·L^{-1} lead (i.e. the recommended maximum concentration for lead in irrigation waters in the United States) is applied at the rate of 1000 mm·m^{-2} of land per year, then a total of 5000 mg of lead will be added annually to each square metre. Assuming the lead is retained in the top 15 cm of soil (bulk density 1500 kg·m^{-3}), lead will accumulate in the soil at a rate of 22.2 mg·kg^{-1} each year. It would thus take only 4.5 years of irrigation at this rate to increase the concentration of lead in the soil by 100 mg·kg^{-1}. Calculations, published previously in Demayo *et al.* (1980), were in error by a factor of 10. More conservative values of 0.2 mg·L^{-1} are recommended for continuous use on all soils, and 2.0 mg·L^{-1} for use on neutral and alkaline fine-textured soils for up to 20 years. These concentrations would result in maximum levels of lead in soil of 88.9 mg·kg^{-1} in 100 years (continuous use on all soils) and 178 mg·kg^{-1} in 20 years (continuous use on neutral and alkaline soils), respectively, based on the assumptions used above.

4.1.3.12 Lithium

4.1.3.12.1 Guideline

The concentration of total lithium in irrigation waters should not exceed 2.5 mg·L^{-1} for continuous use on all soils.

4.1.3.12.2 Summary of Documents

The maximum concentration of lithium in irrigation water recommended in the United States (NAS/NAE 1973) and Australia (Hart 1974) is 2.5 mg·L^{-1} for use on all noncitrus crops. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend this limit. This value may be too high for barley, but data are lacking for the sensitivity of barley to lithium under field conditions.

4.1.3.12.3 Rationale

Literature summarized in NAS/NAE (1973) indicated that most plants grown in nutrient solutions containing lithium could tolerate up to 5 mg·L^{-1}, except for citrus trees, which began to show toxic responses when the water contained 0.06-0.10 mg·L^{-1}. Similarly, barley has been shown to be sensitive to lithium under nutrient culture conditions; growth has been suppressed by concentrations as low as 1 mg·L^{-1} (Davis *et al.* 1978). Growth of cabbage in nutrient solution containing 6.9 mg·L^{-1} lithium was reduced by 31%, compared with control plants (Hara *et al.* 1977). Lithium in concentrations of 3.5 mg·L^{-1} in irrigation water was toxic to sugar beets (El-Sheikh *et al.* 1971). Deactivation of lithium by soils evidently does not occur (NAS/NAE 1973).

4.1.3.13 Manganese

4.1.3.13.1 Guideline

The concentration of total manganese in irrigation water should not exceed 0.2 mg·L^{-1} for continuous use on all soils, and 10.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.13.2 Summary of Documents

The recommended maximum concentration of manganese in irrigation water in Australia is 0.5 mg·L^{-1} (Hart 1974). The recommended limits in the United States are 0.20 mg·L^{-1} for continuous use, and 10.0 mg·L^{-1} on neutral and alkaline soils for up to 20 years (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.13.3 Rationale

Although manganese is an essential element, it can be toxic to crops in acidic soils, including those of the Peace River region of northern Alberta and British Columbia (Hoyt and Nyborg 1971). A toxic response of wheat grown in nutrient solutions containing manganese began to appear when the manganese content of leaves reached 475 mg·kg^{-1} (dry weight), corresponding to about 75 mg·L^{-1} of manganese in the nutrient solution (Fales and Ohki 1982).

4.1.3.14 Mercury

4.1.3.14.1 Guideline

No guideline for mercury in irrigation water is recommended at this time.

4.1.3.14.2 Summary of Documents

No guidelines exist for mercury in irrigation water in the United States (NAS/NAE 1973). In view of the low concentrations of mercury in natural waters (Reeder *et al.* 1979b) and its retention by soils, guidelines for mercury in irrigation water in Canada have not been proposed. As further data pertaining to uptake by crops become available, it may be necessary to establish a guideline. Hart (1984) recommended that the maximum concentration of total mercury in waters intended for continuous irrigation not exceed 2.0 µg·L^{-1}.

4.1.3.14.3 Rationale

Most plants do not readily accumulate mercury, because it is retained strongly by soil (NRCC 1979b; Environment Canada 1984). Neither alfalfa nor radishes, grown in soil treated with mercury compounds, accumulated mercury to levels as high as were present in the soil (NRCC 1979b; Environment Canada 1984). Some mushrooms, however, have been shown to accumulate mercury up to 33 times its concentration in the soil (Stijve and Besson 1976). Solubility and availability of heavy metals for uptake through roots increase as pH values of soil decrease below 6.5; however, organic matter in acidic soils can also bind metals, thereby decreasing their availability for uptake by plants (Spotswood and Raymer 1973).

4.1.3.15 Molybdenum

4.1.3.15.1 Guideline

The concentration of total molybdenum in irrigation water should not exceed 0.01 mg·L^{-1} for continuous use on all soils, or 0.05 mg·L^{-1} for short-term use on acidic soils.

4.1.3.15.2 Summary of Documents

In the United States (NAS/NAE 1973) and Australia (Hart 1974), the recommended maximum concentration of molybdenum in irrigation water is 0.01 mg·L^{-1} for use on all soils. The limit for short-term use on soils that react with molybdenum is 0.05 mg·L^{-1} in the United States. Ontario (Ontario Ministry of the Environment 1984) recommends 0.01 mg·L^{-1} for waters used continuously on all soils and 0.05 mg·L^{-1} for acid fine-textured soils or acid soils with relatively high iron oxide contents. Manitoba (Williamson 1983) recommends 0.01 mg·L^{-1} for all soils.

4.1.3.15.3 Rationale

Plants tolerate tissue levels of molybdenum of several hundred mg·kg^{-1} (dry weight) without adverse effects (Gupta and Lipsett 1981); hence, the risk associated with uptake by crops from soil is for livestock consuming contaminated feed, rather than for the crops themselves. In ruminants, a dietary ratio of copper:molybdenum of at least 2:1 is required to prevent copper deficiency, but ratios of 6:1 to 15:1 are considered more favourable (Gupta 1979). Accumulation of molybdenum by crops is facilitated in alkaline soil through increased anion exchange and is proportional to the concentration of the element in soil (Gupta and Lipsett 1981). Acidic soils react with molybdenum, making it unavailable to plants, but liming of the soil could release it.

If irrigation water containing 0.01 mg·L^{-1} molybdenum (i.e. the recommended concentration for molybdenum in the United States and Australia) were applied at the rate of 1000 mm·m^{-2} of land per year and retained in the surface 15 cm of soil (density 1500 kg·m^{-3}), then the annual increment of molybdenum in the soil would be 0.044 mg·kg^{-1}. In 100 years, a total of 4.4 mg·kg^{-1} could result. This would be within the range of 1.5-5.0 mg·kg^{-1} which was reported by Barshad (1984) to have produced forage crops, containing up to 20 mg·kg^{-1} molybdenum, that caused molybdenosis in cattle. At lower rates of irrigation, such as 100 and 400 mm·a^{-1}, the potential molybdenum concentrations after 100 years would be 0.4 and 1.8 mg·kg^{-1}, respectively.

4.1.3.16 Nickel

4.1.13.16.1 Guideline

The concentration of total nickel in irrigation water in Canada should not exceed 0.2 mg·L^{-1} for continuous use on all soils, or 2.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.16.2 Summary of Documents

The recommended maximum concentration of nickel in irrigation water in the United States is 0.2 mg·L^{-1} for all soils and 2.0 mg·L^{-1} for up to 20 years on neutral fine-textured soils (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits. In Australia, Hart (1984) recommended 0.2 mg·L^{-1} total nickel for continuous use on all soil types.

Taylor, Demayo and Reeder (1979) considered that, in light of the adsorption of nickel by soils and its apparent lack of accumulation in soils when applied at low concentrations, the concentrations recommended in NAS/NAE (1973) could be used as guidelines in Canada.

4.1.3.16.3 Rationale

Some evidence indicates that nickel in small quantities improves the growth of plants, including oats and mustard (Webber 1972). Decreased yields have been demonstrated in oats and mustard exposed to nickel at 50 mg·kg^{-1} of soil (Webber 1972) and in lettuce exposed to 75 mg·kg^{-1} of soil (Mitchell *et al.* 1978). The availability of nickel to plants increases with increasing acidity of soil (Webber 1972). Nickel concentrations did not increase significantly in soil irrigated for 10 years with wastewater containing 0.05 mg·L^{-1} nickel (Sidle *et al.* 1977).

4.1.3.17 Selenium

4.1.3.17.1 Guideline

The concentration of total selenium in irrigation water should not exceed 0.02 mg·L^{-1} for continuous use on all soils, or 0.05 mg·L^{-1} for intermittent use on all soils.

4.1.3.17.2 Summary of Documents

The recommended maximum concentration of selenium in irrigation water, which is intended to protect livestock from toxic levels in forage, is 0.02 mg·L^{-1} for continuous use on all soils in the United States (NAS/NAE 1973) and Australia (Hart 1984). Ontario (Ontario Ministry of the Environment 1984) also recommends this limit. Manitoba (Williamson 1983), in addition to recommending 0.02 mg·L^{-1} for continuous use on all soils, also has recommended 0.05 mg·L^{-1} for up to 20 years to protect medium- to fine-textured soils. Demayo *et al.* (1979b) adopted the NAS/NAE (1973) value as the Canadian guideline, and recommended in addition a maximum concentration of 0.05 mg·L^{-1} for intermittent use on all soils.

4.1.3.17.3 Rationale

The toxicity of selenium to livestock consuming contaminated forage is of more concern with regard to irrigation water than is the toxicity of selenium to the crops themselves. Concentrations of selenium above 5.0 mg·kg^{-1} in feed are toxic to livestock, according to Horvath (1976). Although some plants require selenium for growth and accumulate up to several thousand milligrams per kilogram, most plants do not require selenium and do not usually accumulate more than 50 mg·kg^{-1} (Rosenfeld and Beath 1964). Soil containing selenium at 3 mg·kg^{-1} resulted in concentrations, on a dry weight basis, of 15 and 81 mg·kg^{-1} in the grain of oats and wheat, 18 mg·kg^{-1} in cucumbers and 160 mg·kg^{-1} in cabbage (Hamilton and Beath 1963, 1964).

Plants absorb inorganic selenium as selenate (SeO_4^{2-}), rather than as selenite (SeO_3^{2-}) (Moxon and Olson 1974). Selenium occurs as soluble selenate in alkaline soils, from which it tends to leach with water, and as insoluble selenite complexed with ferric hydroxide in acidic soils (Geering *et al.* 1968).

4.1.3.18 Uranium

4.1.3.18.1 Guideline (Tentative)

The concentration of total uranium in irrigation water should not exceed 0.01 mg·L^{-1} for continuous or intermittent use on all soils, or 0.1 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.18.2 Summary of Documents

No guidelines exist for uranium in irrigation water, either in the United States (NAS/NAE 1973) or in Australia (Hart 1974). The maximum total concentration of 0.2 mg·L^{-1} uranium initially recommended for irrigation waters in Canada (Environment Canada 1983) was in error.

4.1.3.18.3 Rationale

Uranium in water enters plants through the roots, which constitute the most common site of accumulation within the plant (Hamilton 1974). Only a fraction of the uranium in soil is available to plants, as a result of adsorption to soil particles and organic matter (Harmsen and de Haan 1980). Vegetables have been reported to concentrate uranium to levels 100 times those of the irrigating waters (Morishima *et al.* 1977). Yield of wheat was reduced 50% by addition of uranyl nitrate to soil at 50 mg·kg^{-1}; yield was not affected by 10 mg·kg^{-1} (Zhukov and Zudilkin 1971).

If irrigation water containing 0.01 mg·L^{-1} uranium is applied at the rate of 1000 mm·m^{-2} of land per year, then a total of 10 mg of uranium will be added annually to each square metre. Assuming the uranium is retained in the top 15 cm of soil (bulk density 1500 kg·m^{-3}), uranium will accumulate in the soil at a rate of 0.044 mg·kg^{-1} each year. If the soil under irrigation contained an initial uranium concentration of 2 mg·kg^{-1} (Harmsen and de Haan 1980), it would take 182 years for the uranium concentration in the soil to reach the potentially toxic concentration of 10 mg·kg^{-1} at that rate of application. Because only a fraction of the uranium in soil is available for uptake by plants, the time period would be considerably greater than 182 years. A rate of irrigation of 300 mm·a^{-1} would result in an annual accumulation of only 0.013 mg·kg^{-1}, with 600 years required to reach 10 mg·kg^{-1}.

If groundwater containing uranium at 0.1 mg·L^{-1} is used for irrigation, 10 mg·kg^{-1} could be accumulated in soil in 12 or 40 years, using annual application rates of 1000 or 300 mm, respectively.

4.1.3.19 Vanadium

4.1.3.19.1 Guideline

The concentration of total vanadium in irrigation water should not exceed 0.1 mg·L^{-1} for continuous use on all soils, or 1.0 mg·L^{-1} for use up to 20 years on neutral and alkaline fine-textured soils.

4.1.3.19.2 Summary of Documents

The maximum concentration of vanadium in irrigation water recommended in the United States is 0.1 mg·L^{-1} for continuous use; 1.0 mg·L^{-1} is recommended for neutral and alkaline fine-textured soils for a 20-year period (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits.

4.1.3.19.3 Rationale

Vascular plants do not require vanadium for growth; when present in excess, it interferes with absorption of essential elements, including calcium, copper, iron, manganese and phosphorus (Warington 1955; Cannon 1963; Wallace *et al.* 1977). Inhibition of growth begins to appear when vanadium concentrations in soil reach 10 mg·kg^{-1}, depending on soil type and species of plant (Hopkins *et al.* 1977).

4.1.3.20 Zinc

4.1.3.20.1 Guideline

The concentration of total zinc in irrigation waters should not exceed 1.0 mg·L^{-1} for continuous use on soils below pH 6.5; at higher pH, a limit of 5.0 mg·L^{-1} is recommended.

4.1.3.20.2 Summary of Documents

Maximum zinc concentrations of 2.0 mg·L^{-1} in irrigation water used on soils above pH 6, and 1 mg·L^{-1} for acidic sandy soils, were suggested by Pratt (1973). Maximum concentrations of 2.0 mg·L^{-1} for irrigation of soils above pH 6 and 10.0 mg·L^{-1} for neutral or alkaline soils over a 20-year period were recommended for the United States (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend these limits. A maximum of 2.0 mg·L^{-1} in irrigation water is recommended in Australia (Hart 1984).

Taylor and Demayo (1980) concluded from published literature that toxic effects began to appear in plants at zinc concentrations in soil of around 50 mg·kg^{-1}, and that only 1-3% of total zinc in soil is available to plants. Their recommended maximum concentrations of zinc in irrigation waters were 1 mg·L^{-1} for use on soils below pH 6.5 and 5 mg·L^{-1} at higher pH.

4.1.3.20.3 Rationale

Although zinc is essential to the growth of plants, it causes a toxic response by inducing iron deficiency when minimal requirements are exceeded. Zinc deficiency occurred in wheat and barley grown in soil containing zinc at 3.5-6.6 mg·kg^{-1}, whereas maximum yields were attained when zinc concentrations were 160 mg·kg^{-1} for wheat and 95 mg·kg^{-1} for barley. A zinc concentration of 585 mg·kg^{-1} of soil was toxic to swiss chard and spinach, resulting in the accumulation of 800 mg·kg^{-1} in the leaves (Leeper 1978). The toxicity of excess zinc to plants is much greater in acidic soils than in soils above pH 6 (MacLean 1974; MacLean and Dekker 1978). Similarly, the organic content of soils limits the availability of zinc to plants (Spotswood and Raymer 1973).

4.1.4 Pesticides

4.1.4.1 Guideline

There are no data to suggest that insecticide residues in irrigation water that result from registered uses are harmful to crops; therefore, no guidelines are recommended. Herbicide residues should not exceed the concentrations listed in Table 4-9 as toxic to selected crops.

4.1.4.2 Summary of Documents

No guidelines exist for insecticides in irrigation water in the United States (NAS/NAE 1973) or Australia (Hart 1974), because survey data showed maximum concentrations to be below 1.0 μg·L^{-1}. Recommended maximum concentrations of selected herbicides in irrigation water in the United States were given for various crops in tabular format (NAS/NAE 1973); these have been adapted for Canadian crops in Table 4-9.

4.1.4.3 Rationale

Insecticides in surface waters used for irrigation are unlikely to damage crops because they are toxic to animal life, rather than plants, and because they generally occur in surface water in concentrations less than 1 μg·L^{-1} (NAS/NAE 1973; Gummer 1979; Williamson 1984). These low concentrations of residues in water are also considered unlikely to be accumulated by plants to concentrations that would be deleterious to humans or livestock (NAS/NAE 1973).

Herbicides can enter irrigation water in concentrations potentially toxic to crops through treatment of water to control algae and submersed aquatic weeds or treatment of irrigation ditches to control terrestrial weeds. The herbicides registered in Canada for these purposes include acrolein, 2,4-D amine and ester, dalapon, dinoseb, diquat, diuron, chlorofenac, MCPA, paraquat and simazine (Saskatchewan Ministry of the Environment 1984).

The available information on the tolerance of crops to herbicides in irrigation water indicates that concentrations below 1 μg·L^{-1} are not toxic to crops (Table 4-9). Concentrations that are not injurious to crops can be attained by waiting for 5-10 d or by flushing the ditch before using the water for irrigation (Smith *et al.* 1975; Grover *et al.* 1982), as advised on the label of the herbicide. However, caution must be exercised in this practice to avoid potential injury to other sensitive uses. Further data on crop tolerances and persistence of herbicides would assist in management of irrigation water.

4.1.5 Biological Parameters

4.1.5.1 Plant Pathogens

In general, field and orchard crops are vulnerable to a variety of pathogens that can be contracted and transmitted through irrigation water. These pathogens include nematodes, bacteria, fungi and viruses (NAS/NAE 1973). However, in Canada, infestation of crops by pathogens that originate from irrigation water is uncommon. The opportunity for disease

Table 4-9. Tolerance of Crops to Herbicides in Irrigation Water[1]

Herbicide	Application rate	Maximum residues in irrigation water ($\mathrm{mg\cdot L^{-1}}$)	Concentrations known to injure crops ($\mathrm{mg\cdot L^{-1}}$)		References
Applied to water:					
Acrolein	$1.5\ \mathrm{mg\cdot L^{-1}}$	1.5	60	beans, corn, sugar beets	Bruns (1969)
					Yeo (1959)
			20	soybeans	Bruns *et al.* (1964)
Chlorofenac	$14\text{-}20\ \mathrm{kg\cdot ha^{-1}}$	Traces	10	corn	
			0.1	alfalfa	
			0.1-10	sugar beets	
Diquat	$2\text{-}10\ \mathrm{kg\cdot ha^{-1}}$	<0.1	125	corn	
			5	beans	
Paraquat	$1\text{-}2\ \mathrm{kg\cdot ha^{-1}}$	No data	No data		
Simazine	$0.9\ \mathrm{g\cdot m^{-3}}$ water	0.25 and 0.7	0.15	alfalfa, brome grass (eradicated)	Anderson *et al.* (1978)
					Korven (1975)
					Smith *et al.* (1975)
Applied to dry ditches:					
Dalapon	$20\text{-}33\ \mathrm{kg\cdot ha^{-1}}$	<0.2	>7.0	beets	Bruns and Dawson (1959)
			>0.3	corn	
Diuron	$18\text{-}88\ \mathrm{kg\cdot ha^{-1}}$	0.2 and 0.8	No data		Bowmer and Adeny (1978)
Chlorofenac	As above	As above	As above		Grover *et al.* (1982)
Applied to banks only:					
2,4-D amine	$0.8\text{-}3.2\ \mathrm{kg\cdot ha^{-1}}$	0.10	10	corn	Bruns (1954, 1957)
			>1.0	field beans, cucumbers, potatoes, sorghum, alfalfa, peppers	Bruns and Clore (1958)
			0.7	grapes	
			>0.2	sugar beets	
			>0.02	soybeans	
MCPA	$0.9\text{-}2.2\ \mathrm{kg\cdot ha^{-1}}$	No data	No data		

[1] Application rates are registered in Canada for use in ditches or reservoirs and on banks of ditches.

organisms to accumulate to epidemic proportions is minimized because:

1. water is not usually recycled from fields back into the irrigation system for reuse on other crops, thereby controlling the spread of pathogens;
2. irrigation is primarily supplemental and seasonal; thus, irrigation systems are dewatered for long periods and pathogenic organisms are subsequently destroyed; and
3. irrigation water is often of high quality and has not originated from agricultural areas; therefore, there has been little opportunity for contamination.

Although the risk of transmission of pathogens in irrigation water in Canada is low, there has been at least one case where the contamination of water has resulted in the widespread occurrence of a plant pathogen. Collar-rot, *Phytophthora cactorum*, of fruit trees in southern British Columbia occurs in irrigation systems and irrigated soils, but occurs only rarely in nonirrigated soils (McIntosh 1966). Although irrigation is implicated in the spread and maintenance of this disease organism in soils, no relationship between the presence of the organism in water and the incidence of the disease in trees has ever been established.

4.1.5.2 Human and Animal Pathogens and Parasites

4.1.5.2.1 Guideline (Tentative)

Tentative maximum concentrations of 100 fecal coliform bacteria per 100 mL and 1000 total coliform bacteria per 100 mL in irrigation water from surface water or groundwater sources are proposed. These guidelines are designated as tentative in light of discussions on the use of appropriate indicator organisms and concerns are resolved regarding consumption of raw produce which has been irrigated with water containing microbiological agents.

4.1.5.2.2 Summary of Documents

A limit of 1000 fecal coliforms per 100 mL of irrigation water was recommended for use in the United States on all crops, including those eaten raw (NAS/NAE 1973). No microbiological guidelines were proposed in Australia for irrigation water, other than those proposed for use of wastewater in irrigation (Hart 1974). In Manitoba, the maximum acceptable concentration of fecal coliforms in irrigation water is a geometric mean of 1000 per 100 mL, and a maximum of 2000 coliforms per 100 mL in individual samples (Williamson 1983). Ontario recommends that water of the best microbiological quality possible be used. Guidelines of 100 fecal coliforms per 100 mL and 1000 total coliforms per 100 mL are recommended (Ontario Ministry of the Environment 1984).

A distinction must be drawn between contaminated surface water or groundwater and wastewater for use in irrigation. For discussions of the application of wastewater in irrigation, the reviews by Parsons *et al.* (1975) and Environment Canada (1984) should be consulted.

4.1.5.2.3 Rationale

Field crops and vegetables can become contaminated from water containing human and animal pathogens and parasites. These organisms are transferred to the consumer on the surface of the produce, and to animals in their feed. Fecal coliforms are used as indicator organisms to monitor the presence or absence of associated pathogens. This practice is controversial, however, and the recommendation has been made that the predominant fecal coliform bacterium, *Escherichia coli*, should be used as the indicator (Dufour 1977).

A committee of experts reporting to the World Health Organization (WHO 1973) concluded that experience with irrigation of crops using wastewater demonstrated that only a limited risk was associated with effluent containing 100 coliform organisms per 100 mL.

Until such time that an appropriate indicator organism is selected and concerns are resolved regarding the potential problems of consuming raw produce that has been irrigated with water containing coliforms, the Ontario (Ontario Ministry of the Environment 1984) numerical limits are tentatively recommended.

4.1.6 References

Anderson, W.J., J.C. Pringle, R.W. Raines and D.A. Sisneros. 1978. Simazine residue levels in irrigation water after ditchbank application for weed control. J. Environ. Qual. 7: 574-579.

Allison, L.E. 1964. Salinity in relation to irrigation. Adv. Agron. 16: 139-180.

Ayers, R.S. 1977. Quality of water for irrigation. J. Irrig. Drain. Div. Am. Soc. Civ. Eng. 103: 135-154.

Ayers, R.S. and D.W. Westcot. 1976. Water Quality for Agriculture. Irrigation and Drainage Pap. 29. Food and Agriculture Organization of the United Nations, Rome. 97 pp.

Ayers, R.S. and D.W. Westcot. 1985. Water Quality for Agriculture. Irrigation and Drainage Pap. 29 Rev. 1. Food and Agriculture Organization of the United Nations, Rome. 174 pp.

Baker, D.E. 1974. Copper: Soil, water, plant relationships. Fed. Proc. Fed. Am. Soc. Exp. Biol. 33: 1188-1193.

Bale, S.S. and G.E. Hart. 1973a. Studies on cytogenetic and genetic effects of fluoride on barley. I. A comparative study of the effects of sodium fluoride and hydrofluoric acid on seedling root tips. Can. J. Genet. Cytol. 15: 695-702.

Bale, S.S. and G.E. Hart. 1973b. Studies on cytogenetic and genetic effects of fluoride on barley. II. The effects of treatment of seedling coleoptiles with sodium fluoride. Can. J. Genet. Cytol. 15: 703-712.

Barshad, I. 1984. Molybdenum content of pasture plants in relation to toxicity to cattle. Soil Sci. 66: 187-195.

Berg, M.H. 1970. Lead absorption from soil into legumes. J. Minn. Acad. Sci. 36: 96.

Bernstein, L. 1964. Salt Tolerance of Plants. U.S. Dep. Agric. Agric. Res. Serv. Agric. Inf. Bull. 283.

Bernstein, L. 1965. Salt Tolerance of Fruit Crops. U.S. Dep. Agric. Agric. Res. Serv. Agric. Inf. Bull. 292.

Bernstein, L. 1974. Crop growth and salinity. *In* Drainage for Agriculture. J. van Schilfgaarde (ed.). American Society of Agronomy, Madison, Wisconsin. Agron. No. 17. 700 pp.

Bernstein, L., L.E. Francois and R.A. Clark. 1972. Salt tolerance of ornamental shrubs and ground covers. Am. Soc. Hortic. Sci. 97: 550-556.

Bingham, F.T. 1973. Boron in cultivated soils and irrigation waters. *In* Trace Elements in the Environment. E.L. Kothy (ed.). Adv. Chem. Ser. No. 123. pp. 130-138.

Bingham, F.T., A.L. Page, R.J. Mahler and T.J. Ganje. 1975. Growth and cadmium accumulation of plants grown on a soil treated with a cadmium-enriched sewage sludge. J. Environ. Qual. 4: 207-211.

Bollard, E.G. and G.W. Butler. 1966. Mineral nutrition of plants. Annu. Rev. Plant Physiol. 17: 77-112.

Bower, C.A., G. Ogata and J.M. Tucker. 1968. Sodium hazard of irrigation waters as influenced by leaching fraction and by precipitation or solution of calcium carbonate. Soil Sci. 106: 29-34.

Bowmer, K.H. and J.A. Adeny. 1978. Residues of diuron and phytotoxic degradation products in aquatic situations. II. Diuron in irrigation water. Pestic. Sci. 9: 354-364.

Breeze, V.G. 1973. Land reclamation and river pollution problems in the Croal Valley caused by waste from chromate manufacture. J. Appl. Ecol. 10: 513-525.

British Columbia Ministry of Agriculture and Food. 1983. Irrigation Design Manual for Farm Systems in British Columbia. British Columbia Irrigation Committee, Victoria, British Columbia.

Bruns, V.F. 1954. The response of certain crops to 2,4-dichlorophenoxyacetic acid in irrigation water. I. Red Mexican beans. Weeds 3: 359-376.

Bruns, V.F. 1957. The response of certain crops to 2,4-dichlorophenoxyacetic acid in irrigation water. II. Sugar beets. Weeds 5: 250-258.

Bruns, V.F. 1969. Response of sugar beets, soybeans, and corn to acrolein in irrigation water. *In* Proc. Washington State Weed Conf. Agricultural Experiment Service, Washington State University, Pullman, Washington.

Bruns, V.F. and W.J. Clore. 1958. The response of certain crops to 2,4-dichlorophenoxyacetic acid in irrigation water. II. Concord grapes. Weeds 6: 187-193.

Bruns, V.F. and J.H. Dawson. 1959. Effects of DCB-xylene mixtures, amitrol, and sodium salt of dalapon in irrigation water on corn and rutabagas. Weeds 7: 333-340.

Bruns, V.F., R.R. Yeo and H.F. Arle. 1964. Tolerance of Certain Crops to Several Aquatic Herbicides in Irrigation Water. U.S. Dep. of Agriculture. Tech. Bull. No. 1299. 22 pp.

Cameron, D.P. 1985. Saline waters: agricultural uses. *In* Evaluating Saline Waters in a Plains Environment. Plains Aquat. Res. Conf. Proc. D.T. Waite (ed.). University of Regina, Saskatchewan. CPP 17/WSI 14. pp. 75-107.

Cannon, H.L. 1963. The biogeochemistry of vanadium. Soil Sci. 96: 196-204.

Chapman, H.D. (ed.). 1966. Diagnostic Criteria for Plants and Soils. University of California, Berkeley, California. 793 pp.

Chen, Y. and P. Barak. 1982. Iron nutrition of plants in calcareous soils. Adv. Agron. 35: 217-240.

Conover, C.A. and R.T. Poole. 1971. Influence of fluoride on foliar necrosis. Proc. Fl. State Hortic. Soc. 84: 380-383.

Davis, R.D., P.H.T. Beckett and E. Wollan. 1978. Critical levels of twenty potentially toxic elements in young spring barley. Plant Soil 49: 395-408.

Delas, J. 1963. La toxicité du cuivre accumule dans les sols. Agrochimica 7: 258-288.

Demayo, A. and M.C. Taylor. 1981. Copper. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979a. Arsenic. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979b. Selenium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1980. Lead. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Dudas, M.J. and S. Pawluk. 1977. Heavy metals in cultivated soils and in cereal crops in Alberta. Can. J. Soil Sci. 57: 329-339.

Dufour, A.P. 1977. *Escherichia coli*: the fecal coliform. *In* Bacterial Indicators/Health Hazards Associated with Water. A.W. Hoadley and B.J. Dutka (eds.). ASTM Spec. Tech. Publ. 635, Philadelphia, Pennsylvania. pp. 48-58.

Dugdale, P.J. 1978. Cadmium in the lead smelter at Belledune: its association with heavy metals in the ecosystem. *In* Cadmium 77. Proc. 1st Int. Cadmium Conf., Jan. 31 – Feb. 2, 1977, San Francisco, California. pp. 53-75.

Eaton, F.M. 1944. Deficiency, toxicity and accumulation of boron in plants. J. Agric. Res. (Washington, D.C.) 69: 237-277.

Eaton, F.M. 1950. Significance of carbonate in irrigation waters. Soil Sci. 69: 123-133.

El-Sheikh, A.M., A. Ulrich and T.C. Broyer. 1971. Effect of lithium on growth, salt absorption and chemical composition of sugar beet plants. Agron. J. 63: 755-758.

Environment Canada. 1983. Uranium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Environment Canada. 1984. Manual for Land Application of Treated Municipal Wastewater and Sludge. Environmental Protection Programs Directorate, Ottawa. EPS-6-EP-84-1.

Fales, S.L. and K. Ohki. 1982. Manganese deficiency and toxicity in wheat: influence on growth and forage quality of herbage. Agron. J. 74: 1070-1073.

Fisheries and Environment Canada. 1978. Hydrological Atlas of Canada. Compiled by the Canadian National Committee for the International Hydrological Decade. Supply and Services Canada, Ottawa.

Francois, L.E. 1981. Alfalfa management under saline conditions with zero leaching. Agron. J. 73: 1042-1046.

Frank, R., K. Ishida and P. Suda. 1976. Metals in agricultural soils of Ontario. Can. J. Soil Sci. 56: 181-196.

Friberg, L., M. Piscator, G.F. Nordberg and T. Kjellstrom. 1974. Cadmium in the Environment. Chemical Rubber Co. Press Inc., Cleveland, Ohio. 284 pp.

Fuller, W.H. 1977. Movement of Selected Metals, Asbestos, and Cyanide in Soil: Applications to Waste Disposal Problems. U.S. Environmental Protection Agency. EPA-600/2-77-020.

Geering, H.R., E.A. Carey, L.H.P. Jones and W.H. Allaway. 1968. Solubility and redox criteria for the possible forms of selenium in soils. Soil Sci. Soc. Am. Proc. 32: 35-40.

Gough, L.P., H.T. Shacklette and A.A. Case. 1979. Element Concentrations Toxic to Plants, Animals, and Man. U.S. Geol. Surv. Bull. 1466.

Grover, R., L.A. Kerr and A.J. Cessna. 1982. Residues of diuron in irrigation water following fall treatment of the supply canal at soil sterilant rates. *In* Wastes and Prairie Water Quality. 8th Symp. of Water Studies Institute, May 4-5, University of Saskatchewan, Saskatoon.

Gummer, W.D. 1979. Pesticide Residues in Prairie Surface Waters. Water Quality Branch, Inland Waters Directorate, Environment Canada. Unpublished. WQB-80-3.

Gupta, U.C. 1979. Copper in agricultural crops. *In* Biogeochemistry of Copper. J.O. Nriagu (ed.). John Wiley & Sons, New York. pp. 255-288.

Gupta, U.C. and J. Lipsett. 1981. Molybdenum in soils, plants and animals. Adv. Agron. 34: 73-113.

Gupta, U.C., Y.W. Jame, C.A. Campbell, A.J. Leyshon and W. Nicholaichuk. 1985. Boron toxicity and deficiency: A review. Can. J. Soil Sci. 65: 381-409.

Haghiri, F. 1973. Cadmium uptake by plants. J. Environ. Qual. 2: 93-96.

Hamilton, E.I. 1974. The chemical elements and human morbidity – water, air and places – a study of natural variability. Sci. Total Environ. 3: 3-85.

Hamilton, J.W. and O.A. Beath. 1963. Selenium uptake and conversion by certain crop plants. Agron. J. 55: 528-531.

Hamilton, J.W. and O.A. Beath. 1964. Amount and chemical form of selenium in vegetable plants. Agric. Food Chem. 12: 371-374.

Hara, T., Y. Sonada and I. Iwai. 1977. Growth response of cabbage plants to lithium, sodium, and rubidium under water culture conditions. Soil Sci. Plant Nutr. 23: 531-539.

Harmsen, K. and F.A.M. de Haan. 1980. Occurrence and behaviour of uranium and thorium in soil and water. Neth. J. Agric. Sci. 28: 40-62.

Hart, B.T. 1974. A Compilation of Australian Water Quality Criteria. Australian Water Resources Council, Department of Environment and Conservation. Australian Government Publ. Serv., Canberra. Tech. Pap. No. 7.

Hart, B.T. 1984. Australian Water Quality Criteria for Heavy Metals. Australian Water Resources Council, Department of National Development and Energy. Australian Government Publishing Serv., Canberra. Tech. Pap. No. 74.

Hemphill, D.C., C.J. Marienfeld, R.S. Reddy, W.D. Heidlage and J.O. Pierce. 1973. Toxic heavy metals in vegetables and forage grasses in Missouri's lead belt. J. Assoc. Off. Anal. Chem. 56: 994-998.

Hernberg, S. and H. Nordman. 1972. Lead. *In* The Hazards to Health of Persistent Substances in Water. World Health Organization, Regional Office for Europe, Copenhagen. pp. 61-110.

Hopkins, L.L., H.L. Cannon, A.T. Musch, R.M. Welch and F.H. Nielson. 1977. Vanadium. Geochem. Environ. 2: 93-107.

Horvath, D.J. 1976. Trace elements and health. *In* Trace Substances and Health. A Handbook. Part 1. P.M. Newberne (ed.). Marcel Dekker, Inc., New York. pp. 319-356.

Hoyt, P.B. and M. Nyborg. 1971. Toxic metals in acid soils. II. Estimation of plant-available manganese. Soil Sci. Soc. Am. Proc. 35: 241-244.

Huffman, E.W.D. and W.H. Allaway. 1973. Chromium in plants: distribution in tissues, organelles, and extracts, availability of bean leaf Cr to animals. J. Agric. Food Chem. 21: 982-986.

International Commission on Irrigation and Drainage. 1975. Canada. ICID Silver Jubilee Commemorative Volume. New Delhi, India. pp. 184-190.

Jacobs, L.W., D.R. Keeney and L.M. Walsh. 1970. Arsenic residue toxicity to vegetable crops grown on Plainfield sand. Agron. J. 62: 588-591.

Jame, Y.W. 1986. Personal communication. Agriculture Canada, Research Station, Swift Current, Saskatchewan.

Jame, Y.W., W. Nicholaichuk, A.J. Leyshon and C.A. Campbell. 1982. Boron concentration in the soil solution under irrigation: A theoretical analysis. Can. J. Soil Sci. 62: 461-470.

John, M.K. and C. Van Laerhoven. 1972. Lead uptake by lettuce and oats as affected by lime, nitrogen, and sources of lead. J. Environ. Qual. 1: 169-171.

Jones, L.H.P. and C.R. Clement. 1972. Lead uptake by plants and its significance for animals. *In* Lead in the Environment. P. Hepple (ed.). Applied Science Publ., Ltd., Barking, England. pp. 29-33.

Jorgensen, S.E. 1976. An ecological model for heavy metal contamination of crops and ground water. Ecol. Modell. 2: 59-67.

Kearney, T.H. and C.S. Scofield. 1936. The Choice of Crops for Saline Land. U.S. Dep. Agric. Circ. 404, Washington, D.C.

Korven, H.C. 1975. Irrigation ditch maintenance with chemicals and grasses. Can. Agric. Eng. 17: 39-43.

Korven, H.C. and W.E. Randall. 1975. Irrigation on the Prairies. Agriculture Canada. Publication 1488. 26 pp.

Leeper, G.W. 1978. Managing the Heavy Metals on the Land. Pollution Engineering and Technology. Marcel Dekker, Inc., New York. 121 pp.

Maas, E.V. 1985. Salt tolerance of plants. *In* Handbook of Plant Sciences. B.R. Christie (ed.). Chemical Rubber Co. Press Inc., Cleveland, Ohio.

Maas, E.V. and C.J. Hoffman. 1977. Crop salt tolerance—current assessment. J. Irrig. Drain. Div. Am. Soc. Civ. Eng. 130: 115-132.

MacLean, A.J. 1974. Effects of soil properties and amendments on the availability of zinc in soils. Can. J. Soil Sci. 54: 369-378.

MacLean, A.J. and A.J. Dekker. 1978. Availability of zinc, copper and nickel to plants grown in sewage-treated soils. Can. J. Soil Sci. 58: 381-389.

McIntosh, D.L. 1966. The occurrence of *Phytophthora* spp. in irrigation systems in British Columbia. Can. J. Bot. 44: 1591-1596.

McIntyre, C.E. 1981. Serpent River Basin Water Quality Data. 1980. Ontario Ministry of the Environment, Toronto, Ontario.

McKenzie, R.C., C.H. Sprout and N.F. Clark. 1983. Relationship of the yield of irrigated barley to soil salinity as measured by several methods. Can. J. Soil Sci. 63: 519-528.

Miller, J.E., J.J. Hassett and D.E. Koeppe. 1976. Uptake of cadmium by soybeans as influenced by soil cation exchange capacity, pH, and available phosphorus. J. Environ. Qual. 5: 157-160.

Millington, A.J., C.H. Birvill and B. Marsh. 1951. Salt tolerance, germination and growth tests under controlled salinity conditions. J. Agric. West. Aust. 28: 198-210.

Mitchell, G.A., F.T. Bingham and A.L. Page. 1978. Yield and metal composition of lettuce and wheat grown on soils amended with sewage sludge enriched with cadmium, copper, nickel and zinc. J. Environ. Qual. 7: 165-171.

Morishima, H., T. Koga, H. Kawai, Y. Honda and K. Katsurayama. 1977. Studies on the movement and distribution of uranium in the environments – distribution of uranium in agricultural products. J. Radiat. Res. 18: 139-150.

Motto, H.L., R.H. Daines, D.M. Chilko and C.K. Motto. 1970. Lead in soils and plants: Its relationship to traffic volume and proximity to highways. Environ. Sci. Technol. 4: 231-238.

Moxon, A.L. and O.E. Olson. 1974. Selenium in agriculture. *In* Selenium. R.A. Zingaro and W.C. Cooper (ed.). Van Nostrand Reinhold Co., New York. pp. 675-707.

NAS. 1971. Fluorides. Biologic Effects of Atmospheric Pollutants. National Academy of Sciences, Washington, D.C.

NAS. 1974. Chromium. Medical and Biologic Effects of Environmental Pollutants. National Academy of Sciences, Washington, D.C.

NAS. 1977. Arsenic. Medical and Biologic Effects of Environmental Pollutants. National Academy of Sciences, Washington, D.C.

NAS/NAE. 1973. Water Quality Criteria 1972. Report of the U.S. National Academy of Sciences and National Academy of Engineering. Funded by U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

NRCC. 1976. Effects of Chromium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15017. 168 pp.

NRCC. 1978. Effects of Arsenic in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15391. 363 pp.

NRCC. 1979a. Effects of Cadmium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16743. 148 pp.

NRCC. 1979b. Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. 290 pp.

Ontario Ministry of the Environment. 1984. Water Management. Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment. Revised. Toronto, Ontario. 70 pp.

Oster, J.D. and J.D. Rhoades. 1984. Water management for salinity and sodicity control. *In* Irrigation with Reclaimed Municipal Wastewater. A Guidance Manual. California State Water Resources Control Board. Rep. No. 84-1WR. pp. 3-1 to 3-37.

Parsons, D., C. Brownlee, D. Wetter, A. Maurer, E. Haughton, L. Kornder and M. Slezak. 1975. Health Aspects of Sewage Effluent Irrigation. Pollution Control Branch, British Columbia Water Resources Service, Department of Lands, Forests and Water Resources, Victoria, British Columbia. 75 pp.

Pratt, P.F. 1973. Quality Criteria for Trace Elements in Irrigation Water. Univ. Calif. Berkeley Publ. Agric. Sci., Berkeley, California.

Quirk, J.P. 1971. Chemistry of saline soils and their physical properties. *In* Salinity and Water Use. T. Talsma and J.R. Philip (eds.). Macmillan, London. pp. 79-91.

Quirk, J.P. and P.K. Schofield. 1955. The effect of electrolyte concentrations on soil permeability. J. Soil Sci. 6: 163-178.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979a. Cadmium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979b. Mercury. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rhoades, J.D. 1968. Mineral-weathering correction for estimating the sodium hazard of irrigation waters. Soil Sci. Soc. Am. Proc. 32: 648-652.

Rhoades, J.D. 1971. Quality of water for irrigation. Soil Sci. 113: 277-284.

Rose, D. and J.R. Marier. 1978. Environmental Fluoride 1977. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16081. 152 pp.

Rosenfeld, I. and O.A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicology and Nutrition. Academic Press, New York. 411 pp.

Saskatchewan Ministry of the Environment. 1984. A Guide to Aquatic Nuisances and their Control. Water Pollution Control Branch, Regina, Saskatchewan.

Schafer, W.M. 1984. Irrigation Water Quality in Montana. Coop. Ext. Serv. Montguide MT8373.

Shainberg, I. and J.D. Oster. 1978. Quality of Irrigation Water. International Irrigation Information Centre. Volcani Centre, Bet Dagan, Israel.

Sidle, R.C., J.E. Hook and L.T. Kardos. 1977. Accumulation of heavy metals in soils from extended wastewater irrigation. J. Water Pollut. Control Fed. 49: 311-318.

Smith, A.E., R. Grover, G.S. Emmond and H.C. Korven. 1975. Persistence and movement of atrazine, bromacil, monuron, and simazine in intermittently-filled irrigation ditches. Can. J. Plant Sci. 55: 809-816.

Spotswood, A. and M. Raymer. 1973. Some aspects of sludge disposal on agricultural land. Water Pollut. Control 72: 71-77.

Statistics Canada. 1971. 1971 Census of Canada. Agriculture. Canada. Catalogue No. 96-701.

Statistics Canada. 1981. 1981 Census of Canada. Agriculture. Canada. Catalogue No. 96-901.

Stijve, T. and R. Besson. 1976. Mercury, cadmium, lead and selenium content of mushroom species belonging to the genus *Agaricus*. Chemosphere 5: 151-158.

Suarez, D.L. 1981. Relationship between pH_c and sodium adsorption ratio (SAR) and an alternative method of estimating SAR of soil or drainage waters. Soil Sci. Soc. Am. J. 45: 469-475.

Taylor, M.C. and A. Demayo. 1980. Zinc. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., A. Demayo and S.W. Reeder. 1979. Nickel. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., S.W. Reeder and A. Demayo. 1979. Chromium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ter Haar, G. 1970. Air as a source of lead in edible crops. Environ. Sci. Technol. 4: 226-229.

Topham, H.L. 1982. History of Irrigation in Western Canada. Prairie Farm Rehabilitation Administration, Ottawa. 87 pp.

Troughton, M.J. 1975. Atlas of Canadian Agriculture. Portfolio of Maps Based on 1971 Census of Agriculture, University of Western Ontario, London, Ontario.

U.S. EPA. 1976. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023.

U.S. Department of Agriculture. 1954. Diagnosis and Improvement of Saline and Alkali Soils. Salinity Laboratory Staff. USDA Handbook 60. Government Printing Office, Washington, D.C.

Vanselow, A.P. 1966. Cobalt. *In* Diagnostic Criteria for Plants and Soils. H.D. Chapman (ed.). Division of Agricultural Science, University of California, Berkeley, California. pp. 142-156.

Walker, W.M., J.E. Miller and J.J. Hassett. 1977. Effect of lead and cadmium upon the calcium, magnesium, potassium, and phosphorus concentration in young corn plants. Soil Sci. 124: 145-151.

Wallace, A., G.V. Alexander and F.M. Chadbury. 1977. Phytotoxicity of cobalt, vanadium, titanium, silver and chromium. Commun. Soil Sci. Plant Anal. 8: 751-756.

Walsh, L.M., M.E. Sumner and P.B. Corey. 1976. Consideration of soils for accepting plant nutrients and potentially toxic non-essential elements. *In* Land Application of Waste Materials. Soil Conservation Society of America, Ankeny, Iowa. pp. 22-47.

Warington, K. 1955. The influence of iron supply on toxic effects of manganese, molybdenum and vanadium in soybeans, peas and flax. Ann. Appl. Biol. 41: 1-22.

Webber, J. 1972. Effects of toxic metals in sewage on crops. Water Pollut. Control 71: 404-413.

Westcot, D.W. and R.S. Ayers. 1984. Irrigation water quality criteria. *In* Irrigation with Reclaimed Wastewater: A Guidance Manual. California State Water Resources Control Board. Rep. No. 81-1 WR.

WHO. 1973. Reuse of Effluents: Methods of Wastewater Treatment and Health Safeguards. Tech. Rep. Ser. No. 517. World Health Organization, Geneva.

Wilcox, L.V. 1958. Determining the Quality of Irrigation Water. U.S. Dep. Agric. Agric. Res. Serv. Agric. Inf. Bull. No. 197.

Wilcox, L.V. 1960. Boron Injury to Plants. U.S. Dep. Agric. Agric. Res. Serv. Agric. Inf. Bull. No. 21. pp. 3-7.

Williams, R.J.B. and H.H. LeRiche. 1968. The effect of traces of beryllium on the growth of kale, grass, and mustard. Plant Soil 29: 317-326.

Williamson, D.A. 1983. Surface Water Quality Management Proposal. Vol. 1. Surface Water Quality Objectives. Manitoba Dep. of Environment and Workplace Safety and Health, Winnipeg, Manitoba. Water Standards and Studies Rep. No. 83-2.

Williamson, D.A. 1984. A Preliminary Investigation into the Presence of Agricultural Pesticides in the LaSalle and Assiniboine Rivers, Manitoba, Canada. Manitoba Department of Environment and Workplace Safety and Health, Water Standards and Studies Rep. No. 84-5.

Woolson, E.A. 1973. Arsenic phytotoxicity and uptake in six vegetable crops. Weed Sci. 21: 524-527.

Yeo, R.R. 1959. Response of Field Crops to Acrolein. Research Committee, Western Weed Control Conferences, Salt Lake City, Utah. Res. Prog. Rep.

Zhukov, B.I. and N.V. Zudilkin. 1971. Effect of uranium on the yield of spring wheat. Radiobiology (Engl. Transl.) 11: 466-469.

4.2 LIVESTOCK WATERING

4.2.1 Introduction

Water of good quality is an essential component of successful livestock production; poor water quality can result in economic loss to the producer, and an inferior product to the consumer. In certain cases, contaminants in drinking water for livestock could be transferred from livestock to the consumer and might cause a public health problem. For example, *Salmonella* infection is occasionally transferred from livestock to man (Deisch 1970). The reverse may also occur. The following sections condense an extensive literature on contaminants, toxic substances, pathogens and parasites that can occur in water and can result in unthriftiness, morbidity or death in livestock.

A summary of recommended Canadian water quality guidelines for livestock drinking water is presented in Table 4-10. For details regarding the recommended guidelines, the reader is referred to the subsequent discussion appearing in this chapter. When using these guidelines, the following should be taken into consideration:

Table 4-10. Summary – Guidelines for Livestock Drinking Water Quality

Parameter	Guideline (mg·L^{-1})
Major Ions and Nutrients	
Calcium	1000
Nitrate plus nitrite	100
Nitrite alone	10.0
Sulphate	1000
Total dissolved solids (salinity)	3000 (see Table 4-13)
Heavy Metals and Trace Ions[1]	
Aluminum	5.0
Arsenic	0.5 5.0 (when not added to feed)
Beryllium[2]	0.1
Boron	5.0
Cadmium	0.02
Chromium	1.0
Cobalt	1.0
Copper	1.0 (cattle) 5.0 (swine and poultry) 0.5 (sheep)
Fluoride	2.0 1.0 (if feed contains fluoride)
Iron[3]	—
Lead	0.1
Manganese[3]	—
Mercury	0.003
Molybdenum	0.5
Nickel	1.0
Selenium	0.05
Uranium	0.2
Vanadium	0.1
Zinc	50.0
Pesticides	See discussion on guidelines for drinking water, Chapter 1
Biological Parameters	
Blue-green algae	Avoid heavy growths of blue-green algae
Pathogens and parasites	Water of high quality should be used (see Section 4.2.5.2.1)

[1] Guidelines expressed as total concentrations.

[2] Tentative guideline.

[3] No guideline recommended at this time.

1. Guidelines given were taken directly from published Canadian and United States documents on the subject. When these published guidelines appear to be inadequate, a qualifying statement is included. This statement is usually based on recent data that were not considered in previous guideline publications.
2. Guidelines given provide protection for both livestock and consumer. Protection of the most sensitive species of livestock can be presumed, unless otherwise stated.
3. Because the guidelines presented here are developed from minimum toxic effects data minus a safety factor, they provide suitable protection for all types of livestock. When different species of livestock have substantial differences in their tolerance to a particular parameter, the parameter in question is considered on a species-specific basis.

The setting of guidelines for drinking water for livestock consumption is complicated by factors similar to those encountered when guidelines are developed for other water uses. Problems include the lack of conclusive research results on cause-effect relationships between contaminants and animals, the unknown effects of combinations of toxicants or interaction of toxicants with other elements (antagonistic, synergistic or additive), and analytical problems associated with measuring the active component of a toxicant. In addition, guidelines for livestock drinking water must take into account the type of livestock, the daily water requirements of each species (Table 4-11), as well as the concentration of certain elements and compounds added to feed in order to enhance weight gain and reduce risk of disease (Table 4-12). If water for livestock contains elevated concentrations of elements, the diets of the animals may require adjustments to ensure that the elements in question are not being consumed in toxic amounts.

Table 4-11. Average Daily Water Requirements for Livestock

Class of livestock	Daily requirement (L)
Dairy cow	160
Beef cow	55
Feeder pig	7-10
Ewe	2-7
Laying hen	0.25-0.3

Source: Saskatchewan Agricultural Services Co-ordinating Committee 1984.

4.2.2 Major Ions and Nutrients

4.2.2.1 Calcium

4.2.2.1.1 Guideline

Drinking water for livestock should not contain more than 1000 mg·L^{-1} of calcium if calcium is the dominant cation. If other major ions, such as magnesium and sodium, are present at high concentrations, or if calcium is added as a dietary supplement to livestock feeds, then the guideline should be adjusted downward (see Section 4.2.2.4.1).

Table 4-12. Mineral Requirements for Growing and Finishing Steers and Heifers

Mineral	% of dry matter
Calcium	0.18-1.04
Phosphorus	0.18-0.70
Magnesium	0.04-0.10
Potassium	0.60-0.80
Sodium	0.06
Sulphur	0.10
Iron	10[1]
Copper	4[1]
Zinc	20-30[1]
Manganese	1-10[1]
Cobalt	0.05-0.10[1]
Iodine	Small, but unknown

[1] Units are mg·kg^{-1}.

Source: NAS/NRC 1976.

4.2.2.1.2 Summary of Documents

No guidelines are given for calcium in water for livestock in the United States (NAS/NAE 1973; NAS 1974). In Australia, Hart (1974) suggested that livestock drinking water could safely contain calcium as high as 1000 mg·L^{-1}, or 700 mg·L^{-1} if magnesium is present in substantial quantities. The NAS (1980) recommended maximum dietary levels of calcium at 1% for swine, 1.2% for poultry, 4% for laying hens and 2% for cattle, sheep, horses and rabbits, provided that the intake of phosphorus is adequate for utilization of calcium. Calcium at high concentrations may interfere with the absorption of phosphorus in the gastrointestinal tract, and thus the overall dietary calcium load should be considered in relation to phosphorus.

4.2.2.1.3 Rationale

Calcium is beneficial to livestock, and is often given as a dietary supplement when natural sources of calcium are inadequate. High concentrations of calcium in drinking water for livestock have been suspected of contributing to phosphorus deficiency and causing calculus formation (Hart 1974). Calcium in drinking water for livestock does not appear to be a problem, according to NAS (1974), which does not include it among elements considered to be potentially toxic, but discusses only its requirement as a nutrient.

4.2.2.2 Nitrate and Nitrite

4.2.2.2.1 Guideline

The concentration of nitrate plus nitrite as nitrogen (N) in water used for livestock should not exceed 100 mg·L^{-1}. The concentration of nitrite alone should not exceed 10.0 mg·L^{-1} (N).

4.2.2.2.2 Summary of Documents

Maximum concentrations of 100 mg·L^{-1} for nitrate plus nitrite as N and 10.0 mg·L^{-1} for nitrite (N) alone in water for livestock were recommended for the United States (NAS/NAE 1973). These limits were also recommended by Ontario (Ontario Ministry of the Environment 1984). Manitoba recommends limits of 10 mg·L^{-1} for nitrate plus nitrite, 10 mg·L^{-1} for nitrate, 0.05 mg·L^{-1} for nitrilotriacetic acid, and 1.0 mg·L^{-1} for nitrite (Williamson 1983). In Australia (Hart 1974), the recommended maximum concentrations are 90 to 200 mg·L^{-1} for nitrate (as NO_3), depending upon type of livestock, and 10 mg·L^{-1} (as NO_2) for nitrites alone.

4.2.2.2.3 Rationale

Livestock can receive nitrate (NO_3) and nitrite (NO_2) in food and drinking water; hence, both sources must be considered in cases of possible poisoning. No harmful effects were noted among swine given 330 mg·L^{-1} of nitrate-nitrogen (NO_3-N) in their drinking water through two breeding seasons, nor did 100 mg·L^{-1} of nitrite-nitrogen (NO_2-N) in the drinking water of young pigs affect body levels of vitamin A or hemoglobin for 105 d (Seerely *et al.* 1965). Similarly, up to 300 mg·L^{-1} of NO_3 or up to 200 mg·L^{-1} of NO_2-N in water had no adverse effects on chickens; however, growth of turkeys was suppressed by 200 mg·L^{-1} of NO_2-N in their drinking water, but unaffected by 50 mg·L^{-1} NO_2-N (Adams *et al.* 1966). Dairy cattle receiving 374 mg·L^{-1} potassium nitrate in their drinking water for 35 months did not differ from the control group except for a significant reduction in the rate of conception (Kahler *et al.* 1975). Veal calves in the induced anemic state during the last month before slaughter may undergo reduced growth or be killed by concentrations of nitrate in excess of 3 mg·L^{-1} in their drinking water (Rodenburg 1986).

4.2.2.3 Sulphate

4.2.2.3.1 Guideline

Sulphate in water used for livestock should not exceed 1000 mg·L^{-1} as SO_4. Higher concentrations of sulphate can be tolerated, but loss in production should be anticipated. Concentrations of sulphate greater than 500 mg·L^{-1} may accentuate deficiencies of the trace elements, Cu, Zn, Fe or Mn.

4.2.2.3.2 Summary of Documents

Hart (1974) recommended that sulphate should not exceed 1000 mg·L^{-1} in water used for livestock. No guideline is recommended in the United States (NAS/NAE 1973).

4.2.2.3.3 Rationale

At concentrations of 1000 mg·L^{-1}, sulphate causes diarrhea in young animals (Church 1979). However, higher concentrations can be tolerated, but the degree of tolerance depends on the species of livestock, their age, adjustment period, and the principal cations associated with the sulphate ion. From least to most desirable, the major cations associated with sulphate are magnesium < sodium < calcium. Weeth and Hunter (1971) reported diuresis, decreased water and food consumption, and weight loss in Hereford cattle drinking water containing 3380 mg·L^{-1} (as SO_4) sodium sulphate. Digesti and Weeth (1976) reported that the safe tolerance concentration of sodium sulphate in drinking water for Hereford-Angus weanling heifers tested for 90 days was 2500 mg·L^{-1}. Dairy cattle in Ontario showed improved productivity and health when their source of drinking water was changed from deep well water, containing 1500 to 2500 mg·L^{-1} sulphate, to surface ponds in which water contained less than 1000 mg·L^{-1} sulphate (Rodenburg 1986).

4.2.2.4 Total Dissolved Solids (Salinity)

4.2.2.4.1 Guideline

The concentration of total dissolved solids (TDS) in water used for livestock watering should not exceed 3000 mg·L^{-1} (Table 4-13). Water with higher TDS concentrations can be used, but the type of livestock, their age, reproductive state, concentrations of sulphate and magnesium and a calculated loss in production must be considered before water with greater than 3000 mg·L^{-1} should be used. Water with more than 7000 mg·L^{-1} should be avoided as livestock water if possible. Under no circumstances should water with TDS concentrations greater than 10 000 mg·L^{-1} be used for livestock watering.

4.2.2.4.2 Summary of Documents

The maximum concentration of soluble salts recommended in the United States as acceptable in water for livestock is 3000 mg·L^{-1} (NAS/NAE 1973). The same limit is recommended in Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983).

Published guidelines for TDS in drinking water for livestock are outlined in Table 4-13 (NAS/NAE 1973; Hart 1974). Water with 1000 mg·L^{-1} TDS or less is highly desirable for all types of livestock. Water with 1000-3000 mg·L^{-1} TDS may cause some loss in performance, especially if the dominant ions are magnesium or sulphate (Jaster *et al.* 1978). Water with over 1500 mg·L^{-1} TDS may cause ascites (water belly) in turkey poults under 3 weeks of age (Hewitt 1986). Water with TDS concentrations above 3000 mg·L^{-1} is questionable for poultry. Swine do not tolerate water with TDS concentrations greater than 7000 mg·L^{-1}, and older horses, sheep or cattle can only subsist on water with TDS concentrations up to 10 000 mg·L^{-1}. Sheep, cattle or horses can survive on water with TDS concentrations as high as 13 000 mg·L^{-1}, especially if they are acclimated slowly to these concentrations (NAS/NAE 1973). However, TDS concentrations in the 10 000-13 000 mg·L^{-1} range are not recommended for livestock watering under any circumstances. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommended a limit of 3000 mg·L^{-1}.

4.2.2.4.3 Rationale

Excessively saline water, when consumed in large amounts, can cause physiological upset and ultimately death in the majority of terrestrial animals, including humans. For example, TDS concentrations greater than 10 000 mg·L^{-1} are generally not suitable for watering cattle (NAS/NAE 1973; Ayers and Westcot 1976). In most parts of Canada, natural surface waters usually have TDS concentrations well below those considered unsuitable for livestock. Nonetheless, some groundwaters, water from industrial uses and natural waters, primarily in Saskatchewan and Alberta, can be highly saline and in some cases lethal to livestock. In Saskatchewan, surface waters with TDS concentrations greater than 10 000 mg·L^{-1}, and in some cases up to 100 000 mg·L^{-1} or more, have been found (Rawson and Moore 1944; Rutherford 1970). It is probable that a significant proportion of ponds and small lakes in this region are also extremely saline.

Livestock will normally avoid water of high salinity if given the choice, but in certain circumstances they may be forced to drink water of poor quality. Water of marginal quality can cause a loss in overall condition, a reduction in weight gain and a reduction of milk or egg production. The effect of saline water also varies according to age and reproductive state of an animal, and the type of feed (dry or green). Therefore, water of marginal quality should not be used. However, when water of suitable quality is not available, water of marginal quality may be used for short periods of time. Livestock can adjust physiologically to some extent to water of relatively high salinity. This adjustment should occur over several weeks. A sudden change from water of low salinity to water of relatively high salinity can initiate toxic symptoms and in some cases may cause death.

Table 4-13. Guide to the Use of Saline Waters for Livestock Watering

Total soluble salts content of waters (mg·L^{-1})	EC[1]	Suitability for livestock
<1000	<1.5	Relatively low level of salinity; excellent for all classes of livestock
1000-3000	1.5-5	Satisfactory for all classes of livestock and poultry, but some loss in productivity should be anticipated; may cause temporary and mild diarrhea in livestock not accustomed to them or watery droppings in poultry
3000-5000	5-8	Satisfactory for livestock, but may cause temporary diarrhea or be refused at first by animals not accustomed to them; poor waters for poultry, often causing watery feces, increased mortality and decreased growth, especially in turkeys
5000-7000	8-11	Can be used with reasonable safety for beef cattle, sheep, swine and horses; avoid use for pregnant or lactating animals, and dairy cattle; not acceptable for poultry
7000-10 000	11-16	Unfit for poultry and probably for swine; considerable risk in using for pregnant or lactating cows, horses or sheep, or for the young of these species; in general, use should be avoided, although older ruminants, horses, poultry and swine may subsist on them under certain conditions
>10 000	>16	Risks with these highly saline waters are so great that they cannot be recommended for use under any conditions

[1] EC = electrical conductivity.

Source: NAS/NAE 1973.

4.2.3 Heavy Metals and Trace Ions

4.2.3.1 Aluminum

4.2.3.1.1 Guideline

The maximum concentration of aluminum recommended for livestock drinking water is 5.0 mg·L^{-1}, but there is no evidence that concentrations up to an order of magnitude higher would be detrimental to livestock.

4.2.3.1.2 Summary of Documents

It has been recommended that the concentration of aluminum in water used for livestock watering in the United States not exceed 5.0 mg·L^{-1} (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend this limit.

4.2.3.1.3 Rationale

Natural waters usually have aluminum concentrations of less than 1 mg·L^{-1}. At this concentration, aluminum is not harmful or toxic to animals. Except for areas subjected to elevated hydrogen ion concentrations, aluminum concentrations in water should be well below those that might be harmful for livestock watering. No adverse effects were observed when aluminum sulphate was fed to sheep and cows at 15 000 mg·kg^{-1} of diet (Bailey 1977), or when aluminum chloride was fed to steers at 1200 mg·kg^{-1} of diet (Valdivia *et al.* 1978). The NAS (1980) summary of aluminum toxicity suggests that aluminum in the diet at concentrations below 500 mg·kg^{-1} does not have adverse effects on poultry, but concentrations of 500 mg·kg^{-1} or more could be deleterious.

4.2.3.2 Arsenic

4.2.3.2.1 Guideline

The concentration of arsenic in water used by livestock should not exceed 0.5 mg·L^{-1}. This concentration provides a substantial degree of safety, and also allows for arsenic intake from other sources. However, if arsenic is not provided as a food additive and natural levels of arsenic in feed are low, then a maximum concentration of 5.0 mg·L^{-1} could be tolerated without adverse effects on livestock or consumer.

4.2.3.2.2 Summary of Documents

A maximum concentration of 0.2 mg·L^{-1} was recommended for livestock watering in the United States (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) recommends the same limit. Demayo *et al.* (1979a) recommended that arsenic concentrations not exceed 0.5 mg·L^{-1}. Manitoba (Williamson 1983) recommends the same limit. Hart (1984) recommended that the maximum total arsenic concentration in livestock drinking waters in Australia be 0.5 mg·L^{-1}.

4.2.3.2.3 Rationale

Arsenite (trivalent) salts are more toxic than arsenate (pentavalent) salts. The lethal single dose for animals in general is 10-50 mg·kg^{-1} for lead arsenate and 35-100 mg·kg^{-1} for calcium arsenate (NRCC 1978).

Cattle fed arsenic acid at 1.25 mg·kg^{-1} in grain supplement showed no toxic effects or increased accumulation in milk (Peoples 1964). Arsenic trioxide had no adverse effects on rats and mice fed up to 34 mg·L^{-1} in their drinking water for 24 months (Hueper and Payne 1962). The NAS (1980) summary gave a maximum tolerable dietary level for livestock of 50 mg·kg^{-1} of feed for inorganic forms of arsenic and 100 mg·kg^{-1} for organic forms.

Arsenic occurs naturally at low levels in livestock feeds, and organic arsenic compounds are used as feed additives to enhance growth in pigs and poultry (Gough *et al.* 1979).

4.2.3.3 Beryllium

4.2.3.3.1 Guideline (Tentative)

Until additional research identifies safe concentrations of beryllium in water, and in order to provide a degree of safety for animal health, the concentration of beryllium in water used by livestock should not exceed 0.1 mg·L^{-1}.

4.2.3.3.2 Summary of Documents

NAS/NAE (1973) did not recommend a concentration limit for beryllium because of lack of data.

4.2.3.3.3 Rationale

Beryllium can be toxic, may be carcinogenic and has the potential to bioaccumulate (U.S.EPA 1980). Beryllium rickets can be induced in rats, poultry and livestock when beryllium is added to food or water at a minimum concentration of 163 mg·L^{-1} (as Be) beryllium carbonate (Guyatt *et al.* 1933; Kay and Guyatt 1933; Kay and Skill 1934). Beryllium sulphate at a concentration of 0.43 mg·L^{-1} (as Be) given to mice and rats over their lifespan did not affect growth and longevity, but some leukemias and tumours were observed (Schroeder and Mitchener 1975a, b). An application factor of 0.2 (subtle and deleterious effects: Reeder 1979) is applied to the concentration of 0.43 mg·L^{-1} to arrive at a tentative maximum concentration of 0.1 mg·L^{-1}.

4.2.3.4 Boron

4.2.3.4.1 Guideline

The concentration of boron in water used for livestock watering should not exceed 5.0 mg·L^{-1}.

4.2.3.4.2 Summary of Documents

The NAS/NAE (1973) guideline suggests that the boron concentration in water used by livestock should not exceed 5.0 mg·L^{-1}. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) recommend the same limits. There is no evidence that levels several times higher would be detrimental to livestock.

4.2.3.4.3 Rationale

There is no evidence that boron is toxic to livestock at relatively high concentrations. Therefore, there has been little effort to determine toxic concentrations of this element. The

NAS (1980) gave a maximum tolerable level of 150 mg·kg^{-1} boron (as borax) in the diet of cattle, and suggested this value should be reasonable for other species of livestock. In cattle, concentrations of boron at 150 mg·L^{-1} in drinking water resulted in a decrease in hay consumption and weight loss, and the safe tolerance concentration of boron was estimated to be between 40 and 150 mg·L^{-1} (Green and Weeth 1977).

4.2.3.5 Cadmium

4.2.3.5.1 Guideline

The concentration of cadmium in water used by livestock should not exceed 0.02 mg·L^{-1}.

4.2.3.5.2 Summary of Documents

An upper limit of 0.05 mg·L^{-1} was recommended for cadmium in water used for livestock in the United States (NAS/NAE 1973) and Ontario (Ontario Ministry of the Environment 1984). Reeder *et al.* (1979a) recommended that the concentration of cadmium not exceed 0.02 mg·L^{-1}. Manitoba (Williamson 1983) recommends the same limit. The maximum tolerable level of dietary cadmium for livestock, which is designed to minimize cadmium levels in the food supply of consumers, is 0.5 mg·kg^{-1} of feed (NAS 1980). A maximum concentration of 0.01 mg·L^{-1} total cadmium in livestock drinking waters was recommended in Australia (Hart 1984).

4.2.3.5.3 Rationale

Studies using rodents indicate that cadmium could be responsible for a variety of disorders in mammals. Cadmium at high concentrations is not only toxic, but can also be teratogenic and possibly mutagenic and carcinogenic (U.S. EPA 1980).

Anemia, abortions, stillbirths, reduced growth and reduced immune responses were observed in livestock when given doses of cadmium that ranged from 1 to 160 mg·kg^{-1} of body weight (Table 4-14). Cadmium is more toxic if the level of calcium in the diet is low. Cadmium accumulates in the liver and kidneys of livestock as well as other animals. Because these organs are consumed by humans, livestock that have acquired unusually high concentrations of cadmium in these organs could pass toxic levels of cadmium on directly to the consumer.

Table 4-14. Summary of the Effects of High Concentrations of Cadmium on Livestock

Livestock	Cadmium intake in feed	Symptom	Source
Calf	160 mg·kg^{-1}	Reduced growth	Powell *et al.* 1964
Dairy cow	3000 mg·d^{-1}	Reduced milk production	Miller *et al.* 1967
Lamb	30 mg·kg^{-1}	Reduced growth	Doyle *et al.* 1974
Turkey	20 mg·kg^{-1}	Reduced growth	Supplee 1961

4.2.3.6 Chromium

4.2.3.6.1 Guideline

The concentration of chromium in water used by livestock for drinking should not exceed 1.0 mg·L^{-1}. This concentration is probably conservative, given the maximum levels that can be tolerated in feed.

4.2.3.6.2 Summary of Documents

An upper limit of 1.0 mg·L^{-1} was recommended for chromium in water used for livestock watering in the United States (NAS/NAE 1973). In addition, Taylor, Reeder and Demayo (1979) recommended that the concentration of chromium not exceed 1.0 mg·L^{-1}. This limit is also recommended by Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983). Hart (1984) recommended a maximum concentration of 1.0 mg·L^{-1} total chromium in livestock drinking waters in Australia.

4.2.3.6.3 Rationale

Chromium occurs naturally in two forms, Cr(III) and Cr(VI), of which only the latter is highly toxic. The trivalent form of chromium, Cr(III), tends to adsorb on food fibres or precipitate in an insoluble form in the digestive tract.

In rats and dogs, chromium did not accumulate in tissues when drinking water contained concentrations of 5.0-6.0 mg·L^{-1} of Cr(VI). However, chromium at 10 mg·L^{-1} in water accumulated in tissues of these mammals, but was not toxic (NRCC 1976). Chick diets containing 100 mg·kg^{-1} Cr(VI) had no effect on performance over a 21-d period (Romoser *et al.* 1961). Rats with 500 mg·L^{-1} of Cr(VI) as potassium chromate in their drinking water showed no obvious toxic effects (Gross and Heller 1946); similarly, no detrimental effects were observed at 25 mg·L^{-1} (MacKenzie *et al.* 1958). The maximum tolerable dietary intake for domestic animals of Cr(VI) was set in the United States at 3000 mg·kg^{-1} as the oxide and 1000 mg·kg^{-1} as the chloride (NAS 1980).

4.2.3.7 Cobalt

4.2.3.7.1 Guideline

The concentration of cobalt in water used for livestock watering should not exceed 1.0 mg·L^{-1}.

4.2.3.7.2 Summary of Documents

Given the low toxicity of cobalt to animals and its low concentration in the environment, a maximum concentration of 1.0 mg·L^{-1} cobalt in water used by livestock in the United States was felt to provide adequate protection and a margin of safety (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) also recommend this limit.

4.2.3.7.3 Rationale

Cobalt is an essential trace element in several enzyme systems in animals, and is, therefore, of dietary importance. At concentrations well above those found in the natural environment, cobalt is not toxic to animals. For example, calves given cobalt at 1.1 mg·kg^{-1} body weight per day had reduced appetite and some loss in weight (Underwood 1977). Drinking water for calves would have to contain at least 10 mg·L^{-1} cobalt before the symptoms observed by Underwood (1977) would be evident. This value is several orders of magnitude above typical concentrations in surface waters. Swine, cattle and poultry should be able to tolerate at least 10 mg·kg^{-1} cobalt in the diet (NAS 1980).

4.2.3.8 Copper

4.2.3.8.1 Guideline

Taking into consideration the safe dietary intake of copper for livestock, as well as consumer protection, the copper concentration in drinking water should not exceed 1.0 mg·L^{-1} for cattle and 5.0 mg·L^{-1} for swine and poultry. For sheep, a maximum of 0.5 mg·L^{-1} is recommended. However, these levels should be revised downward, especially for sheep, if levels of copper are high in forage plants and in soil, or if copper is regularly given to livestock as a dietary supplement.

4.2.3.8.2 Summary of Documents

A maximum concentration of 0.5 mg·L^{-1} for water used for livestock watering in the United States (NAS/NAE 1973) and Ontario (Ontario Ministry of the Environment 1984) was recommended. Demayo and Taylor (1981) recommended that the copper concentration should not exceed 1 mg·L^{-1} for drinking water for sheep and cattle and 5 mg·L^{-1} for drinking water for swine and poultry. Manitoba (Williamson 1983) recommends a limit of 1.0 mg·L^{-1}. Hart (1984) recommended that the maximum concentration of copper in livestock drinking waters in Australia not exceed 0.5 to 2.0 mg·L^{-1}, depending upon the animals' dietary intake of copper.

4.2.3.8.3 Rationale

Copper is widely used in the livestock industry as a dietary supplement because it is essential to animal health. However, the intake of copper by livestock can have either negative or beneficial effects, depending on its total intake. When natural concentrations of copper are well below the dietary requirements, copper deficiency can occur, particularly in sheep and cattle, and can result in morbidity and in some cases death (NAS 1977). The recognized safe level of copper intake is up to 15 mg·kg^{-1} of feed for most species of livestock. However, somewhat lower levels are preferred for dietary intake by sheep because they are sensitive to copper (Demayo and Taylor 1981).

Copper toxicosis in livestock can occur when forage plants contain high concentrations of copper, or when natural sources and dietary supplements, combined, contain an excess of copper. Toxicosis resulting strictly from intake of copper in drinking water has not been reported, and therefore must be rare. The topic of copper toxicosis is complex because of the number of interactive variables that can enhance or suppress toxic symptoms (NAS 1977; U.S. EPA 1980; Demayo and Taylor 1981). For example, the interaction of copper with molybdenum, sulphate, iron and zinc can greatly reduce the toxic effects of high copper levels in the diet. The copper-molybdenum ratio is important to the dietary utilization of copper, and should not fall below 2:1 for maintenance of animal health. The type of livestock, ruminant or nonruminant, is also important, as is the form of copper. For example, copper chloride is 2-4 times more toxic to sheep than is copper sulphate. Toxic effects of copper have been observed at dietary concentrations as low as 45 mg·kg^{-1} in sheep (Reynolds 1976), 250 mg·kg^{-1} in swine (Lillie *et al.* 1977) and 250 mg·kg^{-1} in broiler chicks (Poupoulis and Jensen 197[illegible]).

Maximum levels of dietary copper for livestock were reviewed by Demayo and Taylor (1981). They suggested that in order to avoid toxicosis, the maximum copper concentration should be approximately 5-20 mg·kg^{-1} in the diet for sheep, 100 mg·kg^{-1} for cattle, 150-400 mg·kg^{-1} for swine and 250-500 mg·kg^{-1} for chickens and turkeys. These levels are similar to those recommended by the NAS (1980), which suggested that the maximum tolerable level of dietary copper, with normal levels of molybdenum, sulphate, zinc and iron, should be 25 mg·kg^{-1} for sheep, 100 mg·kg^{-1} for cattle, 250 mg·kg^{-1} for swine and 300 mg·kg^{-1} for chickens and turkeys. In view of their sensitivity to copper, sheep should be protected from concentrations of copper considered acceptable for cattle. Thus, a maximum concentration of 0.5 mg·L^{-1} is proposed for sheep.

At normal and excess levels in the diet of livestock, copper accumulates primarily in the liver. For example, in sheep, 72-79% of body copper content is found in the liver (Dick 1954). The ability of copper to accumulate in the liver creates a potential hazard to the consumer, especially children, and this hazard should be considered when guidelines for copper concentrations in drinking water for livestock are developed.

4.2.3.9 Fluoride

4.2.3.9.1 Guideline

The concentration of fluoride in the drinking water of livestock should not exceed 2.0 mg·L^{-1}. This limit should be reduced to 1.0 mg·L^{-1} in cases where the feed of animals contains fluoride.

4.2.3.9.2 Summary of Documents

Reviews of the available literature on effects of fluoride in drinking water of livestock indicated no-effect concentrations of 1.0 mg·L^{-1} or higher, and resulted in a recommended limit of 2.0 mg·L^{-1} for livestock drinking water in the United States, with acknowledgement that mottling of teeth might occur at that level (NAS/NAE 1973). Ontario (Ontario Ministry of the Environment 1984) also has recommended a limit of 2.0 mg·L^{-1}.

4.2.3.9.3 Rationale

Although dietary fluoride is beneficial in improving resistance of teeth to decay, it is not a demonstrated essential element (NAS 1971). Fluoride tends to accumulate in bone rather than in soft tissues, and ingestion of amounts in excess of normal environmental concentrations has resulted in tooth damage among growing animals and bone lesions resulting in crippling of older animals, especially cattle (Rose and Marier 1978; CPHA 1979). The major source of excessive concentrations of fluoride in the diet of livestock is vegetation contaminated by aerial deposit in industrial areas (NAS 1971). Studies of dietary intake of soluble fluoride by livestock have shown that no toxic effects resulted from dietary concentrations of 30-50 mg·kg^{-1} for cattle, 70-100 mg·kg^{-1} for sheep and swine and 150-400 mg·kg^{-1} for poultry (NAS 1971). Retarded weight gain was reported, however, for sheep receiving 53-70 mg·kg^{-1} fluoride in the diet for 25 months (Said *et al.* 1977). Cattle have developed mottled teeth when given water containing fluoride at 0.5-0.6 mg·L^{-1}, and erosion of teeth has occurred when drinking water contained up to 3.3 mg·L^{-1} (Hibbs and Thilsted 1983) or 4-5 mg·L^{-1} (Obel 1971).

4.2.3.10 Iron

4.2.3.10.1 Guideline

No guideline for iron in the drinking water of livestock is recommended at this time.

4.2.3.10.2 Summary of Documents

Concentrations of iron that occur in livestock drinking water are relatively low and are not considered of sufficient toxicity to warrant the establishment of guidelines (NAS/NAE 1973).

4.2.3.10.3 Rationale

As an essential element, iron is only toxic to livestock when included in the diet at concentrations greater than 3000 mg·kg^{-1} (NAS/NAE 1973). Concentrations of up to 10 mg·L^{-1} have not affected palatability of water to cattle, but concentrations as low as 0.1 mg·L^{-1} in water given to white veal calves cause increased red colouration of the meat (Rodenburg 1986).

4.2.3.11 Lead

4.2.3.11.1 Guideline

The concentration of lead in water used for livestock watering should not exceed 0.1 mg·L^{-1}.

4.2.3.11.2 Summary of Documents

The recommended upper limit for lead in livestock drinking water in the United States is 0.1 mg·L^{-1} (NAS/NAE 1973). The maximum concentration for lead recommended in Australia is 0.5 mg·L^{-1} (Hart 1984). Ontario (Ontario Ministry of the Environment 1984) recommends a limit of 0.1 mg·L^{-1} whereas Manitoba (Williamson 1983) recommends a limit of 0.5 mg·L^{-1}.

4.2.3.11.3 Rationale

Lead is a toxic element which accumulates in the skeleton to a critical maximum, after which circulating levels increase until poisoning occurs (Hatch 1977; Jaworski 1979). A minimum intake of 6-7 mg·kg^{-1}·d^{-1} has induced toxic response in cattle (Hammond and Aronson 1964); calves were killed by accidental exposure for 30 d to an estimated lead dose of 5-8 mg·kg^{-1}·d^{-1} (Osweiler and Ruhr 1978).

Sheep died following dietary exposure to 5.7 mg·kg^{-1} body weight (James *et al.* 1966), whereas sheep receiving 3 mg·kg^{-1} body weight per day did not accumulate the lead (Jones and Clement 1972). Horses have shown greater sensitivity to lead than have cattle or sheep; chronic poisoning occurred in horses receiving stream and spring water and grass contaminated with lead at concentrations of 0.5-1.0 mg·L^{-1} and 5-20 mg·kg^{-1} (dry weight), respectively (Singer 1976). A no-effect concentration of 0.5 mg·L^{-1} lead in water for livestock has been proposed (NAS/NAE 1973) and substantiated by studies with laboratory animals (Schroeder, Vinton *et al.* 1963; Schroeder, Balassa *et al.* 1965); however, reduced resistance to disease has been caused by low-level intake (Schroeder, Balassa *et al.* 1965; Hemphill *et al.* 1971).

Quantities of lead that accumulate in soft tissues comprise less than 10% of total body burden (Jaworski 1979). One survey of lead concentrations in liver and kidney from Canadian livestock demonstrated a range of 0.5-1.8 mg·kg^{-1} (Prior 1976). Lead concentrations in these tissues, therefore, might exceed acceptable levels for lead in food if livestock are raised in areas contaminated by lead, as was reported for bacon and milk by Hernberg and Nordman (1972).

4.2.3.12 Manganese

4.2.3.12.1 Guideline

No guideline for manganese in the drinking water of livestock is recommended at this time.

4.2.3.12.2 Summary of Documents

An upper limit for livestock water was considered unnecessary in the United States (NAS/NAE 1973).

4.2.3.12.3 Rationale

Natural waters contain manganese at low concentrations as salts which oxidize and precipitate with aeration. An essential element, manganese is low in toxicity unless ingested in excessive amounts (NAS/NAE 1973).

4.2.3.13 Mercury

4.2.3.13.1 Guideline

The concentration of mercury in drinking water for livestock should not exceed 3 μg·L^{-1}.

4.2.3.13.2 Summary of Documents

An upper limit of 0.01 mg·L^{-1} was recommended for mercury in water used for livestock watering in the United States (NAS/NAE 1973). Reeder *et al.* (1979b) recommended a limit of 3 μg·L^{-1}. Ontario (Ontario Ministry of the Environment 1984) recommended a limit of 0.01 mg·L^{-1}. The recommended limit for Manitoba is 3 μg·L^{-1} (Williamson 1983). Hart (1984) recommended that the maximum concentration of total mercury in livestock drinking waters in Australia not exceed 2 μg·L^{-1}.

4.2.3.13.3 Rationale

When critical concentrations of mercury were attained in the brain, signs of poisoning were observed at 2 mg·kg^{-1} in turkeys, 8 mg·kg^{-1} in cattle and 10 mg·kg^{-1} in sheep (Palmer *et al.* 1973). Thermoregulation and survival were impaired among chickens exposed chronically to methylmercury (Thaxton *et al.* 1975). Cattle receiving only 0.48 mg of an ethylmercury compound per kilogram of body weight per day accumulated 100 mg·kg^{-1} in the kidneys in 27 d; sheep kidneys under the same conditions accumulated 120-210 mg·kg^{-1} (Palmer *et al.* 1973).

The accumulation of mercury compounds in the tissues of livestock, primarily in the kidneys and liver (NRCC 1979), poses a health hazard to the animals and to human consumers. The maximum allowable mercury concentration in food for daily human consumption is 0.5 mg·kg^{-1} (Health and Welfare Canada 1971). Chickens receiving mercury at approximately 0.001 mg·kg^{-1}·d^{-1} for 1 year accumulated 0.2-0.4 mg·kg^{-1} mercury in the kidneys (March *et al.* 1974). In order to ensure that edible tissues of chickens do not accumulate more than 0.5 mg·kg^{-1} of mercury, daily intake of mercury by chickens should not exceed 0.001 mg·kg^{-1} body weight. Reeder *et al.* (1979b) applied the formula of Kitamura *et al.* (1976),

$$\text{accumulated mercury} = \text{daily dose} \times \text{biological half-life} \times 1.44$$

to calculate the maximum allowable intake of mercury from water, using the chicken as a model, as follows. The daily water intake by birds is 8% of body weight (or 0.08 L·kg^{-1} of body weight), so the daily dose from water containing 3 µg·L^{-1} is 0.24 µg·kg^{-1} of body weight. Assuming a 70-d biological half-life for methylmercury,

$$\text{accumulated mercury} = 0.24 \times 70 \times 1.44 = 24.2\ \mu g \cdot kg^{-1}$$

Assuming a 4:1 ratio for residues in kidneys compared to whole body (March *et al.* 1974), the mercury concentration in kidney is 4 x 24.2 µg·kg = 0.1 mg·kg^{-1}. Thus, if water accounted for 25% of total mercury intake, kidney concentrations would be 0.4 mg·kg^{-1}.

4.2.3.14 Molybdenum

4.2.3.14.1 Guideline

The concentration of molybdenum in water used for livestock watering should not exceed 0.5 mg·L^{-1}. This concentration is half of that recommended for copper in the diet of cattle, which will assist in maintaining the Cu:Mo ratio near 2:1.

4.2.3.14.2 Summary of Documents

No guideline has been established in the United States for molybdenum in drinking water for livestock (NAS/NAE 1973). In Australia, the recommended maximum concentration of 0.01 mg·L^{-1} in irrigation water was adopted as the maximum for molybdenum in livestock drinking water (Hart 1974). A maximum concentration of 0.08 mg·L^{-1} is under consideration by the Province of British Columbia (Swain 1986).

4.2.3.14.3 Rationale

Although considered to be an essential element, the requirement for molybdenum in the diet of livestock has not been established (NAS/NAE 1973). Its toxicity is closely linked to dietary intake of copper and inorganic sulphate.

Ruminants consuming feed grown in areas having elevated levels of molybdenum in the soil have been adversely affected. Dietary intake of 6.2 mg·kg^{-1} caused abnormal bone development in calves (Smith *et al.* 1975). Forage containing 25.6 mg·kg^{-1} caused diarrhea, weight loss, anemia and some mortality among cattle in a herd in the Swan River Valley, Manitoba (Cunningham *et al.* 1953). Cattle require a Cu:Mo ratio of 2:1 to prevent molybdenum poisoning unless copper in the feed exceeds 13-16 mg·kg^{-1} (NAS 1977). Sheep, swine and poultry are more tolerant of elevated concentrations of molybdenum in the diet than are cattle (NAS 1980).

Ammonium molybdate at a concentration of 50 mg·L^{-1} in the drinking water of calves caused a reduction in the copper concentration in liver, but had no such effect at 10 mg·L^{-1} or lower (Kincaid 1980).

4.2.3.15 Nickel

4.2.3.15.1 Guideline

The concentration of nickel in water for livestock watering should not exceed 1.0 mg·L^{-1}.

4.2.3.15.2 Summary of Documents

The NAS/NAE (1973) did not recommend guidelines for nickel. However, the NAS (1974) recommended a maximum of 1.0 mg·L^{-1} nickel in drinking water for livestock. Ontario (Ontario Ministry of the Environment 1984) has recommended a limit of 1.0 mg·L^{-1}. Taylor, Demayo and Reeder (1979) recommended a maximum nickel concentration of 5.0 mg·L^{-1} in drinking water for livestock in Canada; however, these authors considered the minimum toxic level to be 5.0 mg·L^{-1}, based on the effects on rats (Schroeder and Mitchener 1971). Hart (1984) recommended that the maximum concentration of total nickel in livestock drinking waters in Australia not exceed 5.0 mg·L^{-1}. Manitoba (Williamson 1983) also recommends this limit.

4.2.3.15.3 Rationale

It has been well documented that nickel is essential to the health of livestock (NRCC 1981). Swine, goats, sheep and chicks have undergone deleterious physiological changes while receiving nickel-deficient diets (Anke *et al.* 1974; Nielsen and Ollerich 1974; NRCC 1981).

Suppression of growth was induced by nickel salts in calves receiving 250 mg·kg^{-1} (O'Dell *et al.* 1970) and in chicks receiving 500 mg·kg^{-1} (Weber and Reid 1968). Nickel acetate at 5 mg·L^{-1} in the drinking water of mice over their lifetime was not toxic (Schroeder *et al.* 1964); however, Schroeder and Mitchener (1971) reported that nickel chloride at 5 mg·L^{-1} in the drinking water of rats through three generations resulted in increased mortality among newborn pups and increased numbers of runts. Therefore, the more conservative value of 1 $mg{\cdot}L^{-1}$ (NAS 1974) is recommended as the maximum concentration for livestock drinking water.

4.2.3.16 Selenium

4.2.3.16.1 Guideline

The concentration of selenium in water used for livestock watering should not exceed 0.05 $mg{\cdot}L^{-1}$.

4.2.3.16.2 Summary of Documents

The United States (NAS/NAE 1973) and Australia (Hart 1984) have established upper limits of 0.05 and 0.02 $mg{\cdot}L^{-1}$, respectively, for selenium in drinking water for livestock. Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983) have recommended a limit of 0.05 $mg{\cdot}L^{-1}$. Demayo *et al.* (1979b) recommended a maximum concentration of 0.05 $mg{\cdot}L^{-1}$ in livestock drinking water.

4.2.3.16.3 Rationale

Cattle, sheep, swine and poultry have developed selenium-deficiency conditions when maintained on diets containing selenium at 0.02-0.04 $mg{\cdot}kg^{-1}$ or lower (Oldfield *et al.* 1974; Underwood 1977). Estimated minimal concentrations in the diet of livestock are as low as 0.06 (Underwood 1976) and as high as 0.1-0.2 $mg{\cdot}kg^{-1}$ (NAS/NAE 1973). The element does not concentrate in animal tissues (NAS/NAE 1973). The threshold level of dietary selenium required to induce poisoning is estimated to be 5 $mg{\cdot}kg^{-1}$ (Horvath 1976). Poisoning of livestock has occurred following ingestion of forage grown in selenium-rich soil (Johnson 1976), but there is no evidence of toxic response to selenium in natural waters. Turkey poults and chicks did not experience adverse effects from 1.5 or 2 $mg{\cdot}L^{-1}$ of selenium, respectively, in their drinking water (Cantor *et al.* 1984).

4.2.3.17 Uranium

4.2.3.17.1 Guideline

The concentration of uranium in water used for livestock watering should not exceed 0.2 $mg{\cdot}L^{-1}$.

4.2.3.17.2 Summary of Documents

No guidelines have been recommended for uranium in water for livestock, in either the United States (NAS/NAE 1973) or Australia (Hart 1974). A concentration of 0.2 $mg{\cdot}L^{-1}$ was recommended in Canada for livestock drinking water (Environment Canada 1983).

4.2.3.17.3 Rationale

Although livestock ingest up to 1.56 $mg{\cdot}d^{-1}$ of uranium from forage growing in uranium-enriched pastures (Garner 1963), no cases of toxicity have been documented (Gough *et al.* 1979). Phosphorus supplements fed to dairy cattle may provide up to 16 $mg{\cdot}d^{-1}$ uranium, depending upon the source of phosphate (Reid *et al.* 1977). The minimum dose of uranium estimated to cause slight malaise is 50 $mg{\cdot}d^{-1}$ for sheep and 400 $mg{\cdot}d^{-1}$ for cattle (Garner 1963); application of a 0.1 safety factor results in no-effect doses of 5 and 40 $mg{\cdot}d^{-1}$. Cattle receiving 16 $mg{\cdot}d^{-1}$ in phosphorus and 3 $mg{\cdot}d^{-1}$ from forage could receive up to 20 $mg{\cdot}d^{-1}$ in water, for a total intake of the no-effect dose. Thus, the maximum uranium concentration in water should be 0.2 $mg{\cdot}L^{-1}$, assuming cattle drink 38-110 $L{\cdot}d^{-1}$ (NAS/NAE 1973). This limit would also protect sheep.

4.2.3.18 Vanadium

4.2.3.18.1 Guideline

The concentration of vanadium in water used for livestock watering should not exceed 0.1 $mg{\cdot}L^{-1}$.

4.2.3.18.2 Summary of Documents

The upper limit of 0.1 $mg{\cdot}L^{-1}$ for vanadium in drinking water of livestock was recommended in the United States (NAS/NAE 1973). The same limit is recommended in Ontario (Ontario Ministry of the Environment 1984) and Manitoba (Williamson 1983).

4.2.3.18.3 Rationale

Some evidence suggests that vanadium is an essential element in the diet of laboratory rats and chicks (Hopkins and Mohr 1974), being required for lipid, tooth and bone metabolism. Concentrations of vanadium of 2 $mg{\cdot}L^{-1}$ (as NH_4VO_3) in their drinking water improved the development of growing chicks, compared with those receiving only 0.5 $\mu g{\cdot}L^{-1}$ (Hopkins and Mohr 1971); mice receiving 5 $mg{\cdot}L^{-1}$ as vanadyl sulphate through their lifetime showed no adverse effects (Schroeder and Balassa 1967). Reduced growth rates have been induced in chicks and rats given diets containing vanadium at 13 and 25 $mg{\cdot}kg^{-1}$, respectively (van Zinderen Bakker and Jaworski 1980). Rats and mice given daily oral doses of 0.05 $mg{\cdot}kg^{-1}$ body weight for 3-26 weeks developed impairment of their conditioned reflexes (van Zinderen Bakker and Jaworski 1980).

4.2.3.19 Zinc

4.2.3.19.1 Guideline

The concentration of zinc in water used for livestock watering should not exceed 50.0 $mg{\cdot}L^{-1}$.

4.2.3.19.2 Summary of Documents

Upper limits of 20.0 and 25.0 $mg{\cdot}L^{-1}$ were recommended for zinc in water for livestock in Australia (Hart 1984) and the United States (NAS/NAE 1973), respectively. Ontario (Ontario

Ministry of the Environment 1984) recommends a limit of 25.0 mg·L^{-1}. Taylor and Demayo (1980) recommended a maximum concentration of 50.0 mg·L^{-1}. Manitoba (Williamson 1983) also recommended a limit of 50.0 mg·L^{-1}.

4.2.3.19.3 Rationale

An essential element, zinc is required in the diet of livestock as a component of protein and carbohydrate metabolism, although its specific role in animal systems has not been defined (Kirchgessner *et al.* 1977). Dietary requirements of zinc range from 35 mg·kg^{-1} for poultry and ruminants to 100 mg·kg^{-1} for swine (Underwood 1977). Estimated maximum safe levels of zinc are 500 mg·kg^{-1} for calves; 600 mg·kg^{-1} for sheep; 1000 mg·kg^{-1} for chicks, pigs and mature cattle; and 2000 mg·kg^{-1} for turkeys, expressed as concentration in the diet (Neathery and Miller 1977a).

4.2.4 Pesticides

4.2.4.1 Guideline

The adoption of the Canadian guidelines for pesticides in drinking water (Health and Welfare Canada 1979) as the maximum limits of pesticides in livestock drinking water is recommended as a means of providing a margin of safety for livestock and preventing unacceptable residues in animal products. The guidelines for drinking water are described in Chapter 1.

4.2.4.2 Summary of Documents

The United States recommended that the maximum concentrations recommended for public water supplies be applied to drinking water for livestock (NAS/NAE 1973). The same approach was used for the proposal of guidelines in Australia (Hart 1974).

4.2.4.3 Rationale

Entry of pesticides (insecticides, herbicides, fungicides, nematocides and rodenticides) into surface waters occurs by (1) adsorption to soil particles in runoff water; (2) adsorption to wind-blown soil particles; (3) direct application to water for control of biting flies or aquatic weeds; (4) drift of pesticide spray; (5) wet and dry deposition; (6) spills in or near bodies of water; (7) discharges from pesticide formulating and packaging plants; and (8) careless disposal of waste pesticides or containers.

In general, contamination of surface waters by pesticides is limited to concentrations less than 0.1 mg·L^{-1}, because of (1) the rapid breakdown of most pesticides in soil or water; and (2) the low concentrations in water that result from runoff, aerial drift or direct deposit by aerial spraying of agricultural crops or forests.

The majority of insecticides belong to the chemical categories of carbamates, organophosphates or synthetic pyrethroids, most of which tend to be readily metabolized in warm-blooded animals or by microorganisms in soil and water. In many cases, hydrolysis in water is also rapid. Similarly, many herbicides and fungicides currently registered in Canada do not accumulate in tissues or persist in the environment.

Organochlorine insecticides, including DDT, aldrin, dieldrin, endrin and heptachlor, which cause problems of biomagnification through food webs, are no longer registered in Canada for large-scale application. Because of their extremely low water solubility, these compounds are unlikely to occur in high enough concentrations in livestock drinking water to contribute significantly to accumulation by tissues in livestock (NAS/NAE 1973). The acute oral toxicity of pesticides can be categorized as follows according to Weber (1977):

LD_{50} = 4000-9000 mg·kg^{-1} or more; relatively nonhazardous
LD_{50} = 300-4000 mg·kg^{-1}; slightly hazardous
LD_{50} = 20-300 mg·kg^{-1}; moderately hazardous
LD_{50} = 20 mg·kg^{-1}, or less; hazardous

Herbicides, the most commonly used pesticides in Canada, do not in general constitute a hazard to livestock, especially in the concentrations potentially available in surface waters. Commonly used herbicides (Table 4-15) of relatively low mammalian toxicity include 2,4-D, MCPA, dicamba, diclofop-methyl, glyphosate, propanil, triallate and trifluralin. Bromoxynil and difenzoquat are considered to be moderately hazardous.

Organophosphate and carbamate pesticides, because of the relatively high toxicity of some products to vertebrates, have the potential to poison livestock in cases of significant spills into water supplies or runoff from areas treated at rates greatly in excess of label instructions. Contamination of water would dissipate rapidly, however, and relatively toxic insecticides are tolerated in small doses through the diet (Table 4-16). The summarized data for toxicity of pesticides to animal life (Pimentel 1971; Johnson and Finley 1980; Hudson *et al.* 1984) support the suggestion made in NAS/NAE (1973) that if a surface water supply supports a population of fish, the water should be safe for consumption by livestock because of the relatively high sensitivity of fish.

4.2.5 Biological Parameters

4.2.5.1 Toxic Algae

4.2.5.1.1 Guideline

Livestock should not be watered from lakes, ponds or streams that contain heavy growths of blue-green algae, especially if these waters have a history of blue-green algal toxicity.

4.2.5.1.2 Summary of Documents

The guideline documents of both the United States (NAS/NAE 1973) and Australia (Hart 1974) recommend that livestock be prevented from drinking water containing heavy growths of blue-green algae.

4.2.5.1.3 Rationale

In North America, livestock poisoning and death from blue-green algae occur primarily on the Great Plains during summer. In Alberta and Saskatchewan, toxic symptoms or death from toxic blooms of algae in natural waters are not uncommon (Carmichael *et al.* 1977; Carmichael and Gorham 1978). The economic loss from a poisoning event can be substantial. For

Table 4-15. Acute Toxicities of Technical Active Ingredients of Common Herbicides

Herbicide	Acute oral LD_{50}[1] ($mg \cdot kg^{-1}$)	Reference
Bromoxynil	190	Pimentel 1971
2,4-D	375-1200	NRCC 1978
Dicamba	2900	Pimentel 1971
Diclofop-methyl	557-580	Weed Science Society of America 1983
Difenzoquat	270	Weed Science Society of America 1983
Glyphosate	5600	Weed Science Society of America 1983
MCPA	700-1200	NRCC 1978
Propanil	1384	Weed Science Society of America 1983
Triallate	1100	Weed Science Society of America 1983
Trifluralin	>10 000	Weed Science Society of America 1979

[1] Data for adult laboratory rats.

Table 4-16. Summary of Laboratory Feeding Studies on Toxicity of Technical Active Ingredients of Insecticides to Livestock

Insecticide	Acute oral LD_{50}[1] ($mg \cdot kg^{-1}$)	Highest dosage at which no effect was observed	Reference
Carbaryl	540	Pheasants: 350 $mg \cdot kg^{-1}$ body weight per day for 30 d	Hudson *et al.* 1984
		Japanese quail: 300 $mg \cdot kg^{-1}$ feed for 14 weeks	Bursian and Edens 1979
Carbofuran	11	Cattle[2]: 12-147 $mg \cdot kg^{-1}$ feed	Miles *et al.* 1971
Chlorpyrifos	135	Chickens: 20 $mg \cdot L^{-1}$ in drinking water for 28 d	Marshall and Roberts 1978
Fenitrothion	250	Cattle: 100 $mg \cdot kg^{-1}$ feed for 28 d	Johnson and Bowman 1972
Malathion	480-1500	Chicks: 1000 $mg \cdot kg^{-1}$ feed for 30 d	Rehfeld *et al.* 1969
Methoxychlor	5000-6000	Cattle: 0-14 $mg \cdot kg^{-1}$ feed for 113 d	Gardner and Bailey 1975

[1] Data for adult laboratory rats (Pimentel 1971).

[2] Minor symptoms of nervousness occurred during feeding, and disappeared with subsequent feedings.

example, 34 cattle died from drinking water from an unnamed lake in Saskatchewan in 1975 (Carmichael *et al.* 1977).

Death of livestock can occur within minutes or hours of drinking toxic algae. Signs of poisoning include staggering, muscle fasciculations, gasping respiration, convulsions and, finally, respiratory arrest (Carmichael *et al.* 1977). The quantity of water required to obtain a lethal dose of algal toxin can be small. Carmichael *et al.* (1977) calculated that only 1200 mL of water from a typical toxic bloom would be required to kill a 60-kg calf.

In western Canada, the cyanophytes or blue-green algae responsible for causing death in livestock are *Microcystis aeruginosa*, *Anabaena flos-aquae* and *Aphanizomenon flos-aquae*. These algae are capable of producing several toxins, of which only one has been studied in detail (Carmichael and Gorham 1980; Carmichael and Bent 1981). The toxins contain alkaloids which affect the nervous system and cause suffocation, and polypeptides which lead to rapid degeneration of internal organs.

The circumstances leading up to a poisoning event are complex and unpredictable (Carmichael and Gorham 1981). Some of the factors that contribute to the complexity are as follows:

1. Environmental and morphometric conditions in a water body must be suitable for growth, buoyancy and concentration of high densities of toxigenic species of algae.
2. Algal blooms of cyanophytes can be composed of nontoxic and toxic strains of each species. The toxic strains must be dominant and abundant before there is a hazard.
3. Significant differences in toxicity and density of algal blooms can occur over distances of no more than 10 m at any given time because of the wind-generated currents within a water body, and their "piling up" effect on the algae.
4. In water bodies where livestock have been poisoned by blue-green algae, sublethal or lethal algal toxicity probably recurs each summer, but livestock poisoning may not occur because of the short-term spatial and temporal distribution of the toxic blooms.
5. Different species of livestock have different susceptibilities to algal toxicity (Konst *et al.* 1965; Carmichael and Gorham 1977).

4.2.5.2 Pathogens and Parasites

4.2.5.2.1 Guideline

In intensive and high-density livestock operations only high-quality water should be given to livestock. Water supplies of free-ranging livestock should be monitored for pathogenic organisms, and chlorinated if necessary. Sanitation and manure management should be emphasized in order to prevent contamination of the water supply.

4.2.5.2.2 Summary of Documents

No specific recommendation is made pertaining to pathogens and parasites in the United States guideline document (NAS/NAE 1973). In Australia (Hart 1974), the recommended maximum monthly mean density of fecal coliform bacteria in drinking water for livestock is 1000 per 100 mL, with a maximum of 5000 bacteria per 100 mL.

4.2.5.2.3 Rationale

Reduced growth, morbidity or mortality in livestock can occur from a wide variety of viruses, bacteria, protozoa, nematodes and trematodes (Smith *et al.* 1974). A number of these pathogens and parasites can be transmitted and acquired from water contaminated with manure (Barnett 1975). Experience in Ontario has shown that young dairy calves can contract scours (diarrhea) when their drinking water contains total coliform bacteria counts of more than 1 per 100 mL, whereas older cattle tolerate concentrations of 20-50 coliforms per 100 mL with no adverse effects (Rodenburg 1985). Aside from health problems, water contaminated with bacteria can cause decreased consumption by cattle, resulting in loss of milk production.

Some of the more common pathogenic bacteria that livestock can contract from contaminated drinking water include anthrax (*Bacillus*); black leg; bacillary hemoglobinuria; botulism (*Clostridium* spp.); swine erysipelas (*Erysipelothrix*); brucellosis (*Brucella*); leptospirosis (*Leptospira*); salmonellosis (*Salmonella*); tuberculosis (*Mycobacterium*); and goat and sheep foot rot (*Sphaerophorus nodosus* plus *Spirochaeta penortha*).

Viruses can cause a number of serious pathogenic conditions in livestock. Pathogenic viruses are not usually transmitted by water, but a few can be contracted because of inadequate sanitation resulting in contamination of feed and water. In poultry, infectious bursitis and Newcastle disease could be transmitted through contaminated water supplies.

There are hundreds of different kinds of helminthic parasites that can live in the organs, intestinal tract or muscle tissue of livestock (Smith *et al*. 1974). The majority of livestock have a relatively low incidence of parasitic infection (Martin *et al*. 1974; Bouvry and Rau 1984; Kingscote 1985), but the rate of parasitism can increase when sanitary conditions and preventative measures are inadequate. Most of these do not cause mortality directly, but they reduce the growth rate and vitality of livestock and increase the susceptibility to potentially fatal infectious disease organisms.

The life cycle of parasites of livestock can be direct or indirect. In the former, eggs are excreted from an animal and reinfestation occurs when animals consume water, feed or soil contaminated by eggs. Roundworms, such as *Ascaris* that parasitize cattle, pigs and humans and *Haemonchus* that parasitize sheep, cattle and goats, have this type of life cycle. For a few of the parasites, aquatic invertebrates provide a critical link in their life cycle, although most simply require a moist environment.

Parasite species that have indirect life cycles have one or more intermediate hosts. Cestodes of the genus *Taenia* parasitize cattle and swine in the intermediate stage. The adult lives in carnivores such as the dog and fox. Damp environments favour the survival and transfer of this parasite from one host to the next, although an aquatic environment is not critical to the life cycle. *Taenia* can also infect humans when meat infested with cysts is incompletely cooked. Other tapeworms or cestodes, such as *Moniezia* and *Thysanosoma*, have farm animals as the primary host. Trematodes or flukes spend part of their life cycle in freshwater snails and have to infect livestock to complete the life cycle.

Risk from contracting pathogens and some parasites can be greatly reduced by using high-quality water or treating contaminated water with chlorine. Chlorination should destroy most bacterial and viral pathogens and some parasites. The small cost of chlorination greatly outweighs the risk of economic loss that can occur when herds or flocks become infected. Water should not be contaminated with manure, sewage or surface runoff.

Regional agricultural offices have numerous publications on sanitation and waste management for livestock. These publications should be consulted, and emphasis should be placed on prevention of contamination of water supplies by fecal materials, carrion and other noxious products. Manure should be kept away from feed and water, elevated feed bunks and hay racks should be used, and troughs and water should be kept clean. Water-tight manure storage facilities are highly desirable, because they prevent contamination of both surface and groundwaters.

4.2.6 References

Adams, A.W., R.J. Emerick and C.W. Carlson. 1966. Effects of nitrate and nitrite in the drinking water on chicks, poults and laying hens. Poult. Sci. 45: 1215-1222.

Anke, M., M. Grun, G. Dittrich, B. Groppel and A. Hennig. 1974. Low nickel rations for growth and reproduction in pigs. *In* Trace Element Metabolism in Animals. 2. W.G. Hoekstra, J.W. Suttie, H.E. Ganther and W. Mertz (eds.). University Park Press, Baltimore, Maryland. pp. 715-718.

Ayers, R.S. and D.W. Westcot. 1976. Water Quality for Agriculture. Irrigation and Drainage Pap. 29. Food and Agriculture Organization of the United Nations, Rome. 97 pp.

Ayers, R.S. and D.W. Westcot. 1985. Water Quality for Agriculture. Irrigation and Drainage Pap. 29 Rev. 1. Food and Agriculture Organization of the United Nations, Rome. 174 pp.

Bailey, C.B. 1977. Influence of aluminium hydroxide on the solubility of silicic acid in rumen fluid and the absorption of silicic acid from the digestive tract of ruminants. Can. J. Anim. Sci. 57: 239-244.

Barnett, G.M. 1975. The Soil-plant Nutrient Recycling Complex and Rates of Animal Waste Application. Agriculture Canada, Quebec.

Bouvry, M. and M.E. Rau. 1984. *Paramphistomum* spp. in dairy cattle in Quebec. Can. Vet. J. 25: 353-356.

Bursian, S.J. and F.W. Edens. 1979. The prolonged exposure of Japanese quail to carbaryl and its effects on neurochemical and blood chemical parameters. Bull. Environ. Contam. Toxicol. 21: 144-151.

Cantor, A.H., D.M. Nash and T.H. Johnson. 1984. Toxicity of selenium in drinking water of poultry. Nutr. Rep. Int. 29: 683-688.

Carmichael, W.W. and P.E. Bent. 1981. Hemagglutination method for detection of freshwater cyanobacteria (blue-green algae) toxins. Appl. Environ. Microbiol. 41: 1383-1388.

Carmichael, W.W. and P.R. Gorham. 1977. Factors influencing the toxicity and animal susceptibility to *Anabaena flos-aquae* (Cyanophyta) blooms. J. Phycol. 13: 97-101.

Carmichael, W.W. and P.R. Gorham. 1978. Anatoxins from clones of *Anabaena flos-aquae* isolated from lakes of western Canada. Mitt. Int. Ver. Theor. Angew. Limnol. 21: 285-295.

Carmichael, W.W. and P.R. Gorham. 1980. Freshwater cyanophyte toxins: types and their effects on the use of micro algae biomass. *In* Algae Biomass. G. Shelef and C.J. Soeder (eds.). Elsevier/North-Holland Biomedical Press, New York. pp. 437-448.

Carmichael, W.W. and P.R. Gorham. 1981. The mosaic nature of toxic blooms of cyanobacteria. *In* The Water Environment: Algal Toxins and Health. W.W. Carmichael (ed.). Plenum Publ. Corp., New York. pp. 161-172.

Carmichael, W.W., P.R. Gorham and D.F. Biggs. 1977. Two laboratory case studies on the oral toxicity to calves of the freshwater cyanophyte (blue-green algae) *Anabaena flos-aquae*. Can. Vet. J. 18: 71-75.

Church, D.C. 1979. Digestive Physiology and Nutrition of Ruminants. Vol. 2. Nutrition. O & B Books Inc., Corvallis, Oregon.

CPHA. 1979. Criteria Document in Support of a Drinking Water Standard for Fluoride. Final Report. Canadian Public Health Association, Ottawa.

Cunningham, H.M., J.M. Brown and A.E. Edie. 1953. Molybdenum poisoning of cattle in the Swan River Valley of Manitoba. Can. J. Agric. Sci. 33: 254-260.

Deisch, S.L. 1970. Disease transmission of water borne organisms of animal origin. *In* Agricultural Practices and Water Quality. Iowa State University Press, Ames. pp. 265-285.

Demayo, A. and M.C. Taylor. 1981. Copper. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979a. Arsenic. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979b. Selenium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Dick, A.T. 1954. Studies on the assimilation and storage of copper in crossbred sheep. Austr. J. Agric. Res. 5: 511-544.

Digesti, R.D. and H.J. Weeth. 1976. A defensible maximum for inorganic sulfate in drinking water for cattle. J. Anim. Sci. 42: 1498-1502.

Doyle, J.J., W.H. Pfander, S.E. Grebing and J.O. Pierce. 1974. Effect of dietary cadmium on growth, cadmium absorption and cadmium tissue levels in growing lambs. J. Nutr. 104: 160-166.

Environment Canada. 1983. Uranium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Gardner, D.R. and J.R. Bailey. 1975. Methoxychlor: Its Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14102. 164 pp.

Garner, R.J. 1963. Environmental contamination and grazing animals. Health Phys. 9: 597-605.

Gough, L.P., H.T. Shacklette and A.A. Case. 1979. Element Concentrations Toxic to Plants, Animals, and Man. U.S. Geol. Surv. Bull. 1466.

Green, G.H. and H.J. Weeth. 1977. Response of heifers ingesting boron in water. J. Anim. Sci. 45: 812-818.

Gross, W.G. and V.G. Heller. 1946. Chromates in animal nutrition. J. Ind. Hyg. Toxicol. 28: 52-56.

Guyatt, B.L., H.D. Kay and H.D. Branion. 1933. Beryllium rickets. J. Nutr. 6: 313-324.

Hammond, P.B. and A.L. Aronson. 1964. Lead poisoning in cattle and horses in the vicinity of a smelter. Ann. N.Y. Acad. Sci. 111: 595-611.

Hart, B.T. 1974. A Compilation of Australian Water Quality Criteria. Australian Water Resources Council, Department of Environment and Conservation. Australian Government Publ. Serv., Canberra. Tech. Pap. 7.

Hart, B.T. 1984. Australian Water Quality Criteria for Heavy Metals. Department of National Development and Energy, Australian Water Resources Council. Australian Government Publishing Serv., Canberra. Tech. Pap. No. 77.

Hatch, R.C. 1977. Poisons causing nervous stimulation or depression. *In* Veterinary Pharmacology and Therapeutics. 4th edition. L.M. Jones, N.H. Booth and L.E. McDonald (eds.). Iowa State University Press, Ames. pp. 1185-1242.

Health and Welfare Canada. 1971. The Mercury Message. Dispatch 15. Educational Services, Health Protection Branch, Ottawa.

Health and Welfare Canada. 1979. Guidelines for Canadian Drinking Water Quality 1978. Supply and Services Canada, Hull. 76 pp.

Hemphill, F.E., M.L. Kaeberle and W.B. Buck. 1971. Lead suppression of mouse resistance to *Salmonella typhimurium*. Science 172: 1031-1032.

Hernberg, S. and H. Nordman. 1972. Lead. *In* The Hazards to Health of Persistent Substances in Water. World Health Organization, Regional Office for Europe, Copenhagen. pp. 61-110.

Hewitt, P. 1986. Personal communication. British Columbia Ministry of Agriculture and Food, Victoria, British Columbia.

Hibbs, C.M. and J.P. Thilsted. 1983. Toxicosis in cattle from contaminated well water. Vet. Hum. Toxicol. 25: 253-254.

Hopkins, L.L. and H.E. Mohr. 1971. The biological essentiality of vanadium. *In* Newer Trace Elements in Nutrition. W. Mertz and W.E. Cornatzer (eds.). Marcel Dekker Inc., New York. pp. 195-213.

Hopkins, L.L. and H.E. Mohr. 1974. Vanadium as an essential nutrient. Fed. Proc. Fed. Am. Soc. Exp. Biol. 33: 1773-1775.

Horvath, D.J. 1976. Trace elements and health. *In* Trace Substances and Health. A Handbook. Part 1. P.M. Newberne (ed.). Marcel Dekker, Inc., New York. pp. 319-356.

Hudson, R.H., R.K. Tucker and M.A. Haegele. 1984. Handbook of Toxicity of Pesticides to Wildlife. Fish and Wildlife Service, U.S. Department of the Interior, Washington, D.C. Resource Publ. 153. 90 pp.

Hueper, W.C. and W.W. Payne. 1962. Experimental studies in metal carcinogenesis. Chromium, nickel, arsenic. Arch. Environ. Health 5: 445-462.

James, L.F., V.A. Lazar and W. Binns. 1966. Effects of sublethal doses of certain minerals on pregnant ewes and fetal development. Am. J. Vet. Res. 27: 132-135.

Jaster, E.H., J.D. Schuh and T.N. Wegner. 1978. Physiological effects of saline drinking water on high producing dairy cows. J. Dairy Sci. 61: 66-71.

Jaworski, J.F. 1979. Effects of Lead in the Environment – 1978. Quantitative Aspects. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16736. 779 pp.

Johnson, C.M. 1976. Selenium in the environment. Residue Rev. 62: 101-130.

Johnson, J.C., Jr. and M.C. Bowman. 1972. Responses from cows fed diets containing fenthion or fenitrothion. J. Dairy Sci. 55: 777-782.

Johnson, W.W. and M.T. Finley. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. Fish and Wildlife Service, U.S. Dep. of the Interior, Washington, D.C. Resource Publ. 137.

Jones, L.H.P. and C.R. Clement. 1972. Lead uptake by plants and its significance for animals. *In* Lead in the Environment. P. Hepple (ed.). Applied Science Publ., Ltd., Barking, England. pp. 29-33.

Kahler, L.W., N.A. Jorgensen, L.D. Satter, W.J. Tyler, J.W. Crowley and M.F. Finner. 1975. Effect of nitrate in drinking water on reproductive and productive efficiency of dairy cattle. J. Dairy Sci. 58: 771 (abstract).

Kay, H.D. and B.L. Guyatt. 1933. Experimental rickets as a phosphorus deficiency disease. Nature (London) 131: 468-469.

Kay, H.D. and D.I. Skill. 1934. Beryllium rickets (II). The prevention and cure of beryllium rickets. Biochem. J. 28: 1222-1227.

Kincaid, R.L. 1980. Toxicity of ammonium molybdate added to drinking water of calves. J. Dairy Sci. 63: 608-610.

Kingscote, B. 1985. Leptospirosis in sheep in western Canada. Can. Vet. J. 26: 164-168.

Kirchgessner, M., H.P. Roth, R. Spoerl, A. Schnegg, R.J. Kellner and E. Weigand. 1977. A comparative view on trace elements and growth. Nutr. Metab. 21: 119-143.

Kitamura, S., K. Sumino, K. Hayakawa and T. Shibata. 1976. Dose-response relationship of methylmercury. *In* Effects and Dose-response Relationships of Toxic Metals. G.F. Nordberg (ed.). Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. pp. 262-272.

Konst, H., P.D. Mckercher, P.R. Gorham, A. Robertson and J. Howell. 1965. Symptoms and pathology produced by toxic *Microcystis aeruginosa* NRC-1 in laboratory and domestic animals. Can. J. Comp. Med. Vet. Sci. 29: 221-228.

Lillie, R.J., L.T. Frobish, N.C. Steele and G. Graber. 1977. Effect of dietary copper and tylosin and subsequent withdrawal on growth, hematology and tissue residues of growing-finishing pigs. J. Anim. Sci. 45: 100-107.

MacKenzie, R.D., R.V. Byerrum, C.F. Decker, C.A. Hoppert and R.F. Langham. 1958. Chronic toxicity studies. II. Hexavalent and trivalent chromium administered in drinking water to rats. AMA Arch. Ind. Health 18: 232-234.

March, B.E., R. Soong, E. Bilinski and R.E.E. Jonas. 1974. Effects on chickens of chronic exposure to mercury at low levels through dietary fish meal. Poult. Sci. 53: 2175-2181.

Marshall, W.K. and J.R. Roberts. 1978. The Ecotoxicology of Chlorpyrifos. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16079. 314 pp.

Martin, L.J., H.C. Gibbs and J.W. Pullin. 1974. Gastrointestinal parasites of swine in Quebec. 1. An incidence survey. Can. Vet. J. 15: 72-76.

Miles, J.T., B.J. Demott, S.A. Hinton and M.J. Montgomery. 1971. Effect of feeding carbofuran on the physiology of the dairy cow and on pesticide residues in milk. J. Dairy Sci. 54: 478-480.

Miller, W.J., B. Lampp, G.W. Powell, C.A. Salott and D.M. Blackmon. 1967. Influence of a high level of dietary cadmium on cadmium content in milk, excretion, and cow performance. J. Dairy Sci. 50: 1404-1408.

NAS. 1971. Fluorides. Biologic Effects of Atmospheric Pollutants. National Academy of Sciences, Washington, D.C.

NAS. 1974. Nutrients and Toxic Substances in Water for Livestock and Poultry. National Academy of Sciences, Washington, D.C.

NAS. 1977. Copper. Medical and Biologic Effects of Environmental Pollutants. National Academy of Sciences, Washington, D.C.

NAS. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NAS/NAE. 1973. Water Quality Criteria 1972. Report of the U.S. National Academy of Sciences and National Academy of Engineering. Funded by U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

NAS/NRC. 1976. Nutrient Requirements for Beef Cattle. 5th edition. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Neathery, M.W. and W.J. Miller. 1977a. Tolerance levels, toxicity of essential trace elements for livestock and poultry. Part I. Cattle and sheep. Feedstuffs 49: 18-20.

Neathery, M.W. and W.J. Miller. 1977b. Tolerance levels, toxicity of essential trace elements for livestock and poultry. Part II. Swine and poultry. Feedstuffs 49: 22, 27-28.

Nielsen, F.H. and D.A. Ollerich. 1974. Nickel: a new essential trace element. Fed. Proc. Fed. Am. Soc. Exp. Biol. 33: 1767-1772.

NRCC. 1976. Effects of Chromium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15017. 168 pp.

NRCC. 1978. Phenoxy Herbicides. Their Effects on Environmental Quality with Accompanying Scientific Criteria for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16075. 440 pp.

NRCC. 1979. Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. 290 pp.

NRCC. 1981. Effects of Nickel in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18568. 352 pp.

Obel, A.-L. 1971. A literary review of bovine fluorosis. Acta Vet. Scand. 12: 151-163.

O'Dell, G.D., W.J. Miller, W.A. King, S.L. Moore and D.J. Blackmon. 1970. Nickel toxicity in the young bovine. J. Nutr. 100: 1447-1454.

Oldfield, J.E., W.H. Allaway, H.A. Laitinen, H.W. Lakin and O.H. Muth. 1974. Selenium. *In* Geochemistry and the Environment. Vol. 1. The Relation of Selected Trace Elements to Health and Disease. National Academy of Sciences, Washington, D.C. pp. 57-63.

Ontario Ministry of the Environment. 1984. Water Management. Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment. Revised. Toronto, Ontario. 70 pp.

Osweiler, G.D. and L.P. Ruhr. 1978. Lead poisoning in feeder calves. J. Am. Vet. Med. Assoc. 172: 498-500.

Palmer, J.S., F.C. Wright and M. Haufler. 1973. Toxicologic and residual aspects of an alkyl mercury fungicide to cattle, sheep and turkeys. Clin. Toxicol. 6: 425-437.

Peoples, S.A. 1964. Arsenic toxicity in cattle. Ann. N.Y. Acad. Sci. 111: 644-649.

Pimentel, D. 1971. Ecological Effects of Pesticides on Non-target Species. Office of Science and Technology, Washington, D.C. 220 pp.

Poupoulis, C. and L.S. Jensen. 1976. Effect of high dietary copper on gizzard integrity of the chick. Poult. Sci. 55: 113-121.

Powell, G.W., W.J. Miller, J.D. Morton and C.M. Clifton. 1964. Influence of dietary cadmium level and supplemental zinc on cadmium toxicity in the bovine. J. Nutr. 84: 205-214.

Prior, M.G. 1976. Lead and mercury residues in kidney and liver of Canadian slaughter animals. Can. J. Comp. Med. 40: 9-11.

Rawson, D.S. and J.E. Moore. 1944. The saline lakes of Saskatchewan. Can. J. Res. Sect. D. 22: 141-201.

Reeder, S.W. 1979. Preamble. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979a. Cadmium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979b. Mercury. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rehfeld, B.M., D.E. Pratt and M.L. Sunde. 1969. Effect of various levels of dietary malathion on performance of chicks. Poult. Sci. 48: 1718-1723.

Reid, D.F., W.M. Sackett and R.F. Spalding. 1977. Uranium and radium in livestock feed supplements. Health Phys. 32: 535-540.

Reynolds, P.J. 1976. Red cell stability in sheep fed a high Cu level. J. Anim. Sci. 42: 1585-1586.

Rodenburg, J. 1985. Water quality can affect production and health. Ontario Milk Producer 62(2): 12-14.

Rodenburg, J. 1986. Personal communication. Ontario Ministry of Agriculture and Food, Woodstock, Ontario.

Romoser, G.L., W.A. Dudley, L.J. Machlin and L. Loveless. 1961. Toxicity of vanadium and chromium for the growing chick. Poult. Sci. 40: 1171-1173.

Rose, D. and J.R. Marier. 1978. Environmental Fluoride 1977. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16081. 152 pp.

Rutherford, A.A. 1970. Water Quality Survey of Saskatchewan Surface Waters. Saskatchewan Research Council, Saskatoon.

Said, A.N., P. Slagsvold, H. Bergh and B. Laksesvela. 1977. High fluorine water to wether sheep maintained in pens. Nord. Veterinaermed. 29: 172-180.

Saskatchewan Agricultural Services Co-ordinating Committee. 1984. Guide to Farm Practice in Saskatchewan. University of Saskatchewan, Saskatoon.

Schroeder, H.A. and J.J. Balassa. 1967. Arsenic, germanium, tin and vanadium in mice: effects on growth, survival and tissue levels. J. Nutr. 92: 245-252.

Schroeder, H.A. and M. Mitchener. 1971. Toxic effects of trace elements on the reproduction of mice and rats. Arch. Environ. Health 23: 102-106.

Schroeder, H.A. and M. Mitchener. 1975a. Life-term studies in rats: Effects of aluminum, barium, beryllium, and tungsten. J. Nutr. 105: 421-427.

Schroeder, H.A. and M. Mitchener. 1975b. Life-term effects of mercury, methylmercury, and nine other trace metals on mice. J. Nutr. 105: 452-458.

Schroeder, H.A., W.H. Vinton, Jr. and J.J. Balassa. 1963. Effect of chromium, cadmium and other trace metals on the growth and survival of mice. J. Nutr. 80: 39-47.

Schroeder, H.A., J.J. Balassa and W.H. Vinton, Jr. 1964. Chromium, lead, cadmium, nickel and titanium in mice. Effect on mortality, tumors and tissue levels. J. Nutr. 83: 239-250.

Schroeder, H.A., J.J. Balassa and W.H. Vinton, Jr. 1965. Chromium, cadmium and lead in rats: effects on life span, tumors and tissue levels. J. Nutr. 86: 51-66.

Seerely, R.W., R.J. Emerick, L.B. Embry and O.E. Olson. 1965. Effect of nitrate or nitrite administered continuously in drinking water for swine and sheep. J. Anim. Sci. 24: 1014-1019.

Singer, R.H. 1976. Chronic lead poisoning in horses. *In* Proc. Annu. Meet. Am. Assoc. Vet. Lab. Diagn. Vol. 18. pp. 395-405.

Smith, B.P., G.L. Fisher, P.W. Poulos, Jr. and M.R. Irwin. 1975. Abnormal bone development and lameness associated with secondary copper deficiency in young cattle. J. Am. Vet. Med. Assoc. 166: 682-688.

Smith, H.A., T.C. Jones and R.D. Hunt. 1974. Veterinary Pathology. 4th edition. Lea and Febiger, Philadelphia, Pennsylvania. 1521 pp.

Supplee, W.C. 1961. Production of zinc deficiency in turkey poults by dietary cadmium. Poult. Sci. 40: 827-828.

Swain, L. 1986. Personal communication. Water Management Branch, British Columbia Ministry of the Environment, Victoria, British Columbia.

Taylor, M.C. and A. Demayo. 1980. Zinc. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., A. Demayo and S.W. Reeder. 1979. Nickel. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, M.C., S.W. Reeder and A. Demayo. 1979. Chromium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Thaxton, P., W.P. Yomshomis and G.R. Baughman. 1975. Synergistic relationship of temperature, air velocity and mercury in the chicken. J. Appl. Physiol. 38: 969-973.

Underwood, E.J. 1976. Mineral imbalances in farm animals and their study and diagnosis with isotopic tracers. At. Energy Rev. 14: 591-619.

Underwood, E.J. 1977. Trace Elements in Human and Animal Nutrition. 4th edition. Academic Press, Inc., New York. 545 pp.

U.S. EPA. 1980. Ambient Water Quality Criteria for Copper. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-036.

Valdivia, R., C.B. Ammerman, C.J. Wilcox and P.R. Henry. 1978. Effect of dietary aluminum on animal performance and tissue mineral levels in growing steers. J. Anim. Sci. 47: 1351-1356.

van Zinderen Bakker, E.M. and J.F. Jaworski. 1980. Effects of Vanadium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18132. 94 pp.

Weber, C.W. and B.L. Reid. 1968. Nickel toxicity in growing chicks. J. Nutr. 95: 612-616.

Weber, J.B. 1977. The pesticide scorecard. Environ. Sci. Technol. 11: 756-761.

Weed Science Society of America. 1979. Herbicide Handbook. 4th edition. Champaign, Illinois. 479 pp.

Weed Science Society of America. 1983. Herbicide Handbook. 5th edition. Champaign, Illinois. 515 pp.

Weeth, H.J. and J.E. Hunter. 1971. Drinking of sulfate-water by cattle. J. Anim. Sci. 32: 277-281.

Williamson, D.A. 1983. Surface Water Quality Management Proposal. Vol. 1. Surface Water Quality Objectives. Manitoba Dep. of Environment and Workplace Safety and Health, Winnipeg, Manitoba. Water Standards and Studies Rep. No. 83-2.

5.0 INDUSTRIAL WATER SUPPLIES

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5.0 INDUSTRIAL WATER SUPPLIES

5.1 INTRODUCTION

Most industrial operations require adequate supplies of water, and it is rare when such waters can be drawn from streams, lakes or wells, and utilized without treatment to improve quality. The quality of such waters may affect the product by staining, corrosion, contamination, chemical reaction or biological decomposition. It may affect the equipment by corrosion, scale formation or erosion, and the plant efficiency by tuberculation, sludge formation, scale formation, foaming or biological growths (Hart 1974).

Water quality requirements differ widely among industries in Canada because of the number of uses to which water is put by industry. Within any one particular industry, there may be several different unit processes, each requiring a different quality of water. For example, boiler water, process water, cooling water and water for plant cleaning often require water of specific quality.

The purpose of this chapter is to (1) provide information concerning the major effects that specific water quality parameters have on various industrial processes; and (2) recommend water quality guidelines applicable at the point of use for a number of Canadian industries. This information should provide an understanding of industrial water quality needs and the type of water which will require the minimum of pretreatment to meet those needs.

The discussion of water quality requirements for various Canadian industries has been divided into two sections. The first describes water quality requirements for generic uses which are applicable to a wide variety of industrial sectors. Two specific uses have been included: generic heating or steam generation, and generic cooling, either once-through or recirculating.

The second section deals with the water quality requirements specific to different industries. These industries were selected because they use comparatively large quantities of water and are located throughout Canada. Thus, these industries use a wide variety of waters of different qualities.

The following industrial groupings are used:

- Heating and cooling generation
- Steam electric power generation
- Iron and steel industry
- Pulp and paper industry
- Petroleum industry
- Food and beverage industry
- Chemical and allied industries
- Textile industry
- Tanning and leather industry

Although this classification does not cover all industrial water users in Canada, neglecting such industries as mineral extraction, electroplating, photographic processing and the manufacturing of electronic components, it does, nevertheless, include the largest manufacturing industrial water users.

Tabulated values for water quality requirements as identified from the technical or scientific literature or as supplied by industries themselves are included. Also included are brief justifications or explanations as to why particular parameters were emphasized and why specific guidelines were recommended.

5.2 MAJOR USES OF WATER IN CANADIAN INDUSTRIES

According to 1981 data, 11 Canadian industries, as defined by Statistics Canada's (1980) Standard Industrial Classification, recorded a total water intake of 9936 × 10^6 m^3 (Table 5-1). Of this total intake, 63% was used for cooling, condensing and steam generation, 35% for processing and 2% for sanitary and other uses (Tate and Scharf 1985). Of the 11 industries surveyed, cooling, condensing and steam generation accounted for the largest proportion of industrial water use in 9 industries. The largest water-using industry in Canada, paper and allied products, used most of its new water intake for processing (22% of the total industrial intake) (Tate and Scharf 1985).

5.3 INDUSTRIAL WATER TREATMENT

Some industries are able to use available domestic water supplies without pretreatment; however, many others must rely on water from streams, lakes, underground supplies or estuaries which usually requires some form of pretreatment. In some cases, certain industries have such stringent water quality requirements that pretreatment of the domestic water supply is also warranted. Of a total water intake of 9936 × 10^6 m^3 in 1981 in Canada, 89% was obtained from private freshwater surface sources, 7% from public utilities, 3% from private brackish sources and less than 1% from private fresh groundwater sources (Tate and Scharf 1985).

Water treatment technology has been refined to the point where water of reasonable quality can be treated to the desired level of quality for industrial use. Examples of the types of treatment of intake water for various industrial groups in Canada are given in Table 5-2. Using 1981 data, the most frequently used treatment techniques for intake water were screening (46%), followed by chlorination and disinfection (27%) and filtration (11%) (Tate and Scharf 1985). Although some treatment techniques may be quite costly, these costs are generally not a critical economic factor compared with labour costs, market location, marketing costs and source of other raw materials.

Most industries now recognize the importance of both quantity and quality of raw water. Water reuse, with a resulting decrease in both treatment and the need for additional supplies, is now practised by an increasing number of industries.

Table 5-1. Manufacturing Water Intake by Purpose, 1981

	Water intake (10^6 m^3)				
Industry group	Processing	Cooling, condensing and steam	Sanitary	Other	Total
Food and beverage	129	260	36	5	430
Rubber and plastics	19	32	3	—	54
Textiles	46	76	2	—	124
Wood	20	48	5	—	73
Paper and allied	2188	658	43	10	2899
Primary metals	711	1943	54	11	2719
Metal fabricating	16	12	2	—	30
Transportation equipment	48	52	7	2	109
Nonmetallic mineral products	19	58	3	2	82
Petroleum and coal products	38	516	3	6	563
Chemical and chemical products	195	2614	31	13	2853
Total	3429	6269	189	49	9936

Note: Dashes (—) refer to negligible quantities.
The addition of figures may not be possible because of rounding.

Source: Tate and Scharf 1985.

Table 5-2. Manufacturing Water Intake by Type of Intake Treatment, 1981

	Water intake (10^6 m^3)							
Industry group	Filtration	Chlorination and disinfection	Corrosion and slime control	Screening	Hardness and alkalinity control	Other[a]	Total treatment	Total intake
Food and beverage	48	107	16	43	22	6	242	430
Rubber and plastics	1	3	1	6	4	—	15	54
Textiles	21	38	7	57	15	1	139	124
Wood	5	1	—	29	2	—	37	73
Paper and allied	1027	871	151	1374	209	131	3 763	2899
Primary metals	145	1121	672	1714	24	288	3 964	2719
Metal fabricating	3	—	—	1	1	—	5	30
Transportation equipment	—	5	1	52	2	—	60	109
Nonmetallic mineral products	1	8	1	28	1	—	39	82
Petroleum and coal products	25	155	120	459	36	38	833	563
Chemical and chemical products	143	1065	63	2008	86	29	3 394	2853
Treatment totals	1420	3374	1032	5762	403	493	12 491	9936

Note: Dashes (—) refer to negligible quantities.
The addition of figures may not be possible because of rounding.

[a] Includes processes, such as dechlorination and distillation, which are not easily classified.

Source: Tate and Scharf 1985.

5.4 GENERIC PROCESSES

5.4.1 Heating

Efficient operation of process heating systems requires that heat-transfer surfaces are free of corrosion, scale and biological fouling. The quality of water required for process heating or steam generation is dependent on the saturated steam drum pressure and the type of steam generator, as the operating pressure is the prime factor which dictates the chemical makeup of the water, the normal cycles of feedwater concentration, silica volatility and carry-over tendency. The differences between steam and water densities decrease with increasing pressure and temperature; hence, the difficulty of separating the phases completely in the boiler drum increases accordingly. It is necessary to maintain lower boiler water concentrations to maintain the same purity target, as the tendency to carry over is greater at higher operating pressures (Simon and Fynsk 1980).

The major chemical parameter affecting steam purity is the total dissolved solids content of the boiler water; this includes factors which affect surface tension, such as alkalinity and the presence of organic compounds or oily matter. The ability of steam bubbles to break cleanly at the drum water level is inhibited; hence, the entrainment of droplets of boiler water into the steam is promoted. This type of mechanical carry-over predominates at operating pressure ranges below 6.80 MPa. It is important to avoid entrainment of any dissolved solids which could be deleterious to the steam's subsequent use (Simon and Fynsk 1980).

Some chemicals are carried into the steam by volatilization, especially as the operating pressure and temperature rise. Silica is of particular significance. Silica volatilization becomes important at operating pressures above 4.14 MPa. Deposition of silicate scales in the steam generator should not occur if sufficient hydroxide alkalinity is maintained in the boiler water (Simon and Fynsk 1980).

The guidelines for steam generators with current design boilers are itemized in Tables 5-3 to 5-6. These generators have locally high heat fluxes up to 473.2 $kW \cdot m^{-2}$ (150 000 $BTU \cdot h^{-1} \cdot ft^{-2}$), potentially uncertain circulation because of physical size restrictions, relatively small diameter steam drums and small furnaces. For older design units without these constraints, it is often possible to use water of lower quality. These exceptions are indicated in the notes accompanying the tables. The guidelines also apply to steam generators in continuous or relatively steady-state operation. Special operating conditions, such as start-up, shutdown, rapidly fluctuating swing loads or initial operation of new boilers, may dictate the use of higher-quality water (American Society of Mechanical Engineers 1979).

Table 5-7 summarizes the water quality parameters of concern and the difficulties they may cause in water used for heating. In many industries there is a close relationship between the process or product which is being heated or which consumes steam and the types of heater or steam generator used. Thus, it is often difficult to separate the water quality requirements as a result of heating equipment design and those of subsequent processes which consume the steam.

5.4.2 Cooling

Cooling water systems consist of heat-exchange equipment which is used to remove heat from process fluids. Such systems can be classified as once-through and recirculating.

5.4.2.1 Once-through Systems

Whereas the water quality problems associated with once-through systems are similar to those of recirculating systems, they differ in severity and type of treatment. The mineral content of the water does not change significantly, because little evaporation occurs in the system. Because water experiences a small temperature rise in most single-pass heat exchangers, scale problems are slight. But fouling can be substantial, even with a water that is only slightly turbid, because large quantities of water are used (Krisher 1978).

Once-through systems are often constructed of corrosion-resistant metals, such as copper alloys, stainless steel or titanium. Although initially costly, this built-in corrosion resistance can be cost-effective, as little treatment of cooling water is needed. For mild-steel heat exchangers, however, the treatment of water in once-through systems to effectively control corrosion is expensive (Krisher 1978).

Other major problems associated with once-through cooling systems are usually the result of settling of suspended solids, such as silt, clay, sand, corrosion products, aluminum, microbiological debris, process leakage and other suspended material, carried by the cooling water. These materials can adversely affect heat transfer and may result in corrosion beneath the deposits because of the formation of differential concentration cells. Mineral-scale deposition may also occur on heat-transfer surfaces where the solubility of calcium carbonate is exceeded because of local elevated temperature.

Biofouling is caused by the attachment of macro- and microorganisms to surfaces. A slime bacteria layer that has gathered silt and other particulate matter of only 25-μm thickness will retard heat transfer by as much as 10%. Slime bacteria layers of thickness greater than 100 μm (visible to the naked eye) will reduce heat-transfer efficiency by at least 50%. Lack of adequate microbiological control will allow corrosive bacteria to multiply. To prevent the development of biofilms, a biocide application program is required (Krisher 1978).

5.4.2.2 Recirculating Systems

There are two types of recirculating systems: closed and semiclosed. The cooling water in a closed recirculating system is confined within the system's pipes and heat exchangers. The heat absorbed from the plant processes is generally dissipated by air cooling (Krisher 1978).

The most familiar examples of closed cooling systems are refrigeration units, electric generators and chilled-water systems. These are all almost totally sealed. Except for leaks, recirculating cooling water is not lost from the system, and so relatively little makeup water need be added. Overall, the mineral content remains virtually constant, because little evaporation occurs (Krisher 1978).

The cooling water in a semiclosed recirculating system is completely confined within the system's pipes and heat exchangers, except at the cooling tower, where the cooling water is sprayed over a grid. Such systems routinely purge 5-10% of the water flow on a continuous basis, and have a continuous makeup which matches the evaporation plus the purge. The mineral content of these systems would continually increase without the purge, because of a concentration of salts resulting from evaporation (Kerr 1986).

5.4.3 Cooling System Problems

The most serious problems that cooling systems exhibit are corrosion and corrosion-product fouling which forms deposits throughout the heat exchangers or piping (Krisher 1978).

Cooling system problems vary only in degree, and are dependent on the water used and the construction materials contacted. They relate primarily to the system heat exchangers, but also occur in all the system components that come into contact with the cooling water (Krisher 1978).

Deposit problems are usually divided into two types: fouling and scaling. Fouling is the result of accumulation of water-suspended materials on heat-exchanger surfaces. This contributes to equipment deterioration and interferes with heat transfer. Scale is a dense coating of predominantly inorganic material that results from supersaturation and precipitation of water-soluble minerals. This also interferes with heat transfer, thus reducing efficiency (Krisher 1978).

Scale, the most serious barrier to heat transfer, occurs when soluble salts are precipitated and deposited from cooling water. The rate of formation depends on (1) temperature; (2) alkalinity or acidity; and (3) the concentration of salts in the water (Krisher 1978).

Table 5-3. Water Quality Guidelines for Steam Generators. I. Industrial Watertube Including Superheater, Turbine Drives or Process Restriction

	Concentration ($mg \cdot L^{-1}$)							
Drum operating pressure (MPa)[a]	0-2.07	2.08-3.10	3.11-4.14	4.15-5.17	5.18-6.21	6.22-6.89	6.90-10.34	10.35-13.7
Feedwater[b]								
Dissolved oxygen measured before oxygen scavenger addition[c]	<0.04	<0.04	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007
Total iron	≤0.100	≤0.050	≤0.030	≤0.025	≤0.020	≤0.020	≤0.010	≤0.010
Total copper	≤0.050	≤0.025	≤0.020	≤0.020	≤0.015	≤0.015	≤0.010	≤0.010
Total hardness	≤0.300	≤0.300	≤0.200	≤0.200	≤0.100	≤0.050	ND	ND
pH (25°C)	7.5-10.0	7.5-10.0	7.5-10.0	7.5-10.0	7.5-10.0	8.5-9.5	9.0-9.6	9.0-9.6
Chemicals for preboiler system protection	—	—	—	—	—	Use only volatile alkaline materials		
Nonvolatile TOC[d]	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Oily matter	<1	<1	<0.5	<0.5	<0.5	<0.2	<0.2	<0.2
Boiler water								
Silica	≤150	≤90	≤40	≤30	≤20	≤8	≤2	≤1
Total alkalinity (as $CaCO_3$)	<350 [e]	<300 [e]	<250 [e]	<200 [e]	<150 [e]	<100 [e]	NS [f,g]	NS [f]
Free hydroxide alkalinity (as $CaCO_3$)[h]	NS	NS	NS	NS	NS	NS	ND [f,i]	ND [f]
Specific conductance ($\mu S \cdot cm^{-1}$) at 25°C without neutralization	<3500 [j]	<3000 [j]	<2500 [j]	<2000 [j]	<1500 [j]	<1000 [j]	≤150	≤100

Note: Boiler type: Industrial watertube, high duty, primary fuel fired, drum type.

Makeup water percentage: Up to 100% of feedwater.

Conditions: Includes superheater, turbine drives or process restriction on steam purity.

Saturated steam purity target: No values given because steam purity achievable depends upon many variables, including boiler water total alkalinity and specific conductance as well as design of boiler, steam drum internals, and operating conditions (footnotes h and j). Because boilers in this category require a relatively high degree of steam purity, other operating parameters must be set as low as necessary to achieve this high purity for protection of the superheaters and turbines and/or to avoid process contamination.

[a] With local heat fluxes of less than 473.2 $kW \cdot m^{-2}$, use values for the next higher pressure range.

[b] Boilers below 6.21 MPa with large furnaces, large steam release space and internal chelant, polymer and/or antifoam treatment can sometimes tolerate higher concentrations of feedwater impurities than those in the table and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a more positive solution. Alternatives must be evaluated as to practicality and economics in each individual case.

[c] Values in table assume existence of a deaerator.

[d] TOC = total organic carbon. Nonvolatile TOC is that organic carbon not intentionally added as part of the water treatment regime.

[e] Maximum total alkalinity consistent with acceptable steam purity. If necessary, should override conductance as blowdown control parameter. If makeup water is demineralized at 4.14-6.80 MPa, boiler water alkalinity and conductance should be that in table for 6.90-10.34 MPa range.

[f] Refers to free sodium or potassium hydroxide alkalinity. Some small variable amount of total alkalinity will be present and measurable with the assumed congruent or coordinated phosphate-pH control or volatile treatment employed at these high pressure ranges.

[g] NS = not specified.

[h] Minimum level of OH^- alkalinity in boilers below 6.21 MPa must be individually specified with regard to silica solubility and other components of internal treatment.

[i] ND = not detected.

[j] Maximum values often not achievable without exceeding suggested maximum total alkalinity, especially in boilers below 6.21 MPa with 20% makeup water whose total alkalinity is 20% of TDS naturally or after pretreatment by lime soda, or sodium cycle ion exchange softening. Actual permissible conductance values to achieve any desired steam purity must be established for each case by careful steam purity measurements. Relationship between conductance and steam purity is affected by too many variables to allow its reduction to a simple list of tabulated values.

Source: American Society of Mechanical Engineers 1979.

Table 5-4. Water Quality Guidelines for Steam Generators. II. Industrial Watertube Without Superheater, Turbine Drives or Process Restriction

	Concentration ($mg \cdot L^{-1}$)	
Drum operating pressure (MPa)	0-2.07	2.08-3.10
Feedwater[a]		
Dissolved oxygen measured before chemical oxygen scavenger addition[b]	<0.04	<0.04
Dissolved oxygen measured after chemical oxygen scavenger addition[c]	<0.007	<0.007
Total iron	<0.10	<0.050
Total copper	<0.05	<0.025
Total hardness (as $CaCO_3$)	<0.5	<0.3
pH (25°C)	7.0-10.5	7.0-10.5
Nonvolatile TOC[d]	<1	<1
Oily matter	<1	<1
Boiler water		
Silica	<150	<90
Total alkalinity (as $CaCO_3$)	<1000 [e]	<850 [e]
Free hydroxide alkalinity (as $CaCO_3$)[f]	NS [g]	NS
Specific conductance ($\mu S \cdot cm^{-1}$) at 25°C without neutralization	<8000 [e]	<6500 [e]

Note: Boiler type: Industrial watertube, high duty, primary fuel fired, drum type.
Makeup water percentage: Up to 100% of feedwater.
Conditions: No superheater, turbine drives or process restriction on steam purity.
Saturated steam purity target: 1.0 $mg \cdot L^{-1}$ TDS maximum. Target value represents steam purity which should be achievable if other tabulated water quality values are maintained. The target is not intended to be nor should it be construed to represent a boiler performance guarantee. TDS = total dissolved solids.

[a] Boilers with relatively large furnaces, large steam release space and internal chelant, polymer, and/or antifoam treatment can often tolerate higher levels of feedwater impurities than those in the table and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a more positive solution. Alternatives must be evaluated as to practicality and economics in each individual case. The use of some dispersant and antifoam internal treatment is typical in this type of boiler operation so it can tolerate higher feedwater hardness than the boilers in Table 5-3.

[b] Value in table assumes existence of a deaerator.

[c] Chemical deaerator must be provided in all cases but especially if mechanical deaeration is nonexistent or inefficient.

[d] Nonvolatile total organic carbon (TOC) is that organic carbon not intentionally added as part of the water treatment regime.

[e] Alkalinity and conductance values consistent with steam purity target. Practical limits above or below tabulated values can be established for each case by careful steam purity measurements.

[f] Minimum level of OH^- alkalinity must be individually specified with regard to silica solubility and other components of internal treatment.

[g] NS = not specified.

Source: American Society of Mechanical Engineers 1979.

Table 5-5. Water Quality Guidelines for Steam Generators. III. Industrial Firetube Without Superheater, Turbine Drives or Process Restrictions

	Concentration ($mg \cdot L^{-1}$)
Drum operating pressure (MPa)	0-2.07
Feedwater[a]	
Dissolved oxygen measured before chemical oxygen scavenger addition[b]	<0.04
Dissolved oxygen measured after chemical oxygen scavenger addition[c]	<0.007
Total iron	<0.10
Total copper	<0.05
Total hardness (as $CaCO_3$)	<1.0
pH (25°C)	7.0-10.5
Nonvolatile TOC[d]	<10
Oily matter	<1
Boiler water	
Silica	<150
Total alkalinity (as $CaCO_3$)	<700 [e]
Free hydroxide alkalinity (as $CaCO_3$)[f]	NS [g]
Specific conductance ($\mu S \cdot cm^{-1}$) at 25°C without neutralization	<7000 [e]

Note: Boiler type: Industrial firetube, high duty, primary fuel fired.
Makeup water percentage: Up to 100% of feedwater.
Conditions: No superheater, turbine drives, or process restriction on steam purity.
Saturated steam purity target: 1.0 $mg \cdot L^{-1}$ TDS maximum. Target value represents steam purity which should be achievable if other tabulated water quality values are maintained. The target is not intended to be nor should it be construed to represent a boiler performance guarantee. TDS = total dissolved solids.

[a] Firetube boilers of conservative design, with internal chelant, polymer and/or antifoam treatment can often tolerate higher levels of feedwater impurities than those in the table (0.5 $mg \cdot L^{-1}$ Fe, 0.2 $mg \cdot L^{-1}$ Cu, 10 $mg \cdot L^{-1}$ total hardness) and still achieve adequate deposition control and steam purity. Removal of these impurities by external pretreatment is always a more positive solution. Alternatives must be evaluated as to practicality and economics in each individual case.

[b] Value in table assumes existence of a deaerator.

[c] Chemical deaerator must be provided in all cases but especially if mechanical deaeration is nonexistent or inefficient.

[d] Nonvolatile total organic carbon (TOC) is that organic carbon not intentionally added as part of the water treatment regime.

[e] Alkalinity and conductance values consistent with steam purity target. Practical limits above or below tabulated values can be established for each case by careful steam purity measurements.

[f] Minimum level of OH^- alkalinity must be individually specified with regard to silica solubility and other components of internal treatment.

[g] NS = not specified.

Source: American Society of Mechanical Engineers 1979.

Table 5-6. Water Quality Guidelines for Steam Generators. IV. Industrial Coil-type Watertube.

	Concentration ($mg \cdot L^{-1}$)				
Operating pressure (MPa)	0-2.07	2.08-3.10	3.11-4.14	4.15-6.21[a]	≥6.22[a]
Steam purity targets[b]					
Specific conductance at 25°C ($\mu S \cdot cm^{-1}$)	≤50	≤24	≤20	≤0.5	≤0.2
Dissolved solids	≤25	≤12	≤10	≤0.25	≤0.1
Silica	—	—	—	≤0.003	≤0.002
Feedwater[c]					
Dissolved oxygen measured before chemical oxygen scavenger addition[d]	<0.2	<0.2	<0.2	<0.007	<0.007
Dissolved oxygen measured after chemical oxygen scavenger addition[e]	<0.007	<0.007	<0.007	<0.003	<0.003
Total iron	<1.0	<0.3	<0.1	≤0.05	≤0.02
Total copper	<0.1	<0.05	<0.03	≤0.02	≤0.02
Total hardness (as $CaCO_3$)	<1.0	<0.7	<0.5	ND[f]	ND
pH (25°C)	9.0-9.5	9.0-9.5	8.8-9.2	8.8-9.2	8.8-9.2
Chemicals for preboiler system protection	—	—	—	Use only volatile alkaline materials	
Boiler water[g]					
Silica	≤150	≤100	≤60	≤30	≤10 [h]
Total alkalinity (as $CaCO_3$)	<800	<600	<500	<200	<100[h]
Hydroxide alkalinity (as $CaCO_3$)[i]	<300	<200	<120	<60	<50[h]
Specific conductance ($\mu S \cdot cm^{-1}$) at 25°C without neutralization	<8000	<6000	<5000	<4000	<500[h]

Note: Boiler type: Industrial coil-type watertube, primary fuel fired rapid steam generators.
Makeup water percentage: Up to 100% of feedwater.
Total evaporation: Up to 95% of feedwater.
Steam to water ratio (volume to volume): Up to 4000:1. Saturated steam purity target: See table above.

[a] Demineralization of makeup water is recommended.

[b] Tabulated values based on assumption of no superheaters or turbine drives. If steam is used for superheat or turbine drives, use values for ≥6.22 MPa. If unit operation approaches superheat conditions within coil, use values for 4.15-6.21 MPa to avoid silica deposition on near-dry surfaces. The target is not intended to be nor should it be construed as a boiler performance guarantee.

[c] Feedwater defined as makeup water plus condensate, other than separator returns.

[d] Values in the table assume the use of a deaerator.

[e] Chemical deaerator with catalyzed oxygen scavenger is necessary in all cases because feedwater temperature limits imposed by manufacturers of coil-type steam generators preclude efficient mechanical deaeration. Feed of chemical oxygen scavenger must be sufficient to maintain a detectable residual in the boiler water. For those units which include steam separator – water storage drums and recirculate substantial amounts of boiler water, oxygen scavenger residuals should be maintained in higher ranges typical of those employed for drum type boilers.

[f] ND = not detected.

[g] Boiler water analyses determined on separator discharges and/or on storage drum sample.

[h] Suggested values vary with operating pressure, decreasing proportionally as pressure increases up to 17.24 MPa.

[i] Hydroxide alkalinity in $mg \cdot L^{-1}$ $CaCO_3$ must be maintained at a minimum of 1.7 times silica in $mg \cdot L^{-1}$ SiO_2 to keep silica soluble and avoid complex silicate deposits. Most coil-type steam generators do not employ scale control internal treatment chemicals to assist in prevention of such deposits.

Source: American Society of Mechanical Engineers 1979.

Table 5-7. Effects of Some Water Quality Parameters on Heating Equipment

Parameter	Effects on heating equipment
Colour	The colour-causing constituents may cause foaming in boilers. Hinders precipitation methods such as iron removal and softening.
Hardness	Chief source of scale in heat-exchange equipment, boilers, pipelines, etc.
Alkalinity	Foaming and carry-over of solids with steam. Embrittlement of boiler steel. Bicarbonate and carbonate produce CO_2 in steam, a source of corrosion in condensate lines.
Free mineral acids	Corrosion.
Carbon dioxide	Corrosion in water lines and particularly steam and condensate lines.
Sulphate	Adds to solids content of water but in itself is not usually significant. Combines with calcium to form calcium sulphate scale.
Chloride	Adds to solids content and increases corrosive character of water.
Nitrate	Adds to solids content but is not usually significant industrially. Useful for control of boiler-metal embrittlement.
Silica	Scale in boilers and cooling water systems. Insoluble turbine blade deposits because of silica vaporization.
Iron	Discolours water on precipitation. Source of deposits in water lines, boilers, etc.
Manganese	Discolours water on precipitation. Source of deposits in water lines, boilers, etc.
Oxygen	Corrosion of water lines, heat-exchange equipment, boilers, return lines, etc.
Hydrogen sulphide	Cause of "rotten egg" odour. Corrosion.
Ammonia	Corrosion of copper and zinc alloys by formation of complex soluble iron.
Dissolved solids	Process interference and cause foaming in boilers.
Suspended solids	Cause deposits in heat-exchange equipment, boilers, water lines, etc.

Source: American Society of Mechanical Engineers 1979.

Scale forms in the following situations:

1. when water temperature increases as it passes through a heat exchanger, causing a decrease in the solubility of dissolved materials such as calcium sulphate, calcium phosphate, and calcium carbonate. These deposits usually occur first in the cooling-system heat exchangers, where the temperature is the highest and solubilities are lowest.
2. when the bicarbonate alkalinity and calcium hardness of circulating water increase.
3. when water becomes oversaturated with silica or any other scale-forming compound (American Society of Mechanical Engineers 1979).

Calcium carbonate is the most common scale found in cooling water systems; its severity depends on the (calcium) hardness and (bicarbonate) alkalinity of the cooling water. The rate of scaling increases with increasing pH and temperature (Krisher 1978).

Calcium carbonate scale formation can be predicted with empirical scaling indices, such as the Langelier Saturation Index and the Ryznar Stability Index. The Langelier Saturation Index (SI) will produce either a positive or negative value, indicating whether calcium carbonate scale will form (+) or will not form (−) under the conditions being evaluated. The Ryznar Stability Index (RSI) yields positive values (see Section 6.2.11) (Krisher 1978).

Calcium sulphate scale can occur from water containing high concentrations of $CaSO_4$. Calcium sulphate becomes less soluble with decreasing pH and increasing temperature, but precipitates only after all the carbonate has been removed from solution as $CaCO_3$ (Krisher 1978).

The recommended upper limit of calcium and sulphate concentrations in circulating water, in the absence of a scale-inhibiting chemical, is expressed by the formula:

$$[Ca^{2+}] \times [SO_4^{2-}] = 500\,000$$

However, because high concentrations of sulphate and hardness are often accompanied by elevated chloride concentrations, calcium sulphate solubility can be higher than expected. When chloride concentrations exceed 5000 $mg{\cdot}L^{-1}$, an alternative is to limit calcium hardness to 700 $mg{\cdot}L^{-1}$ (as $CaCO_3$) regardless of sulphate concentrations (Krisher 1978).

Calcium phosphate scale is the reaction product of calcium and orthophosphate, and can occur when a phosphate-based treatment is added to cooling water as a corrosion inhibitor. Phosphate may also be present if untreated water is used for makeup. Calcium phosphate is less soluble at higher pH and temperature, and can cause scaling at low concentrations of approximately 5 $mg{\cdot}L^{-1}$ of phosphate in cooling water ($pH > 7.0$ and hardness 500 $mg{\cdot}L^{-1}$ as $CaCO_3$). The scale-formation tendency of calcium phosphate can be calculated if the amount of calcium hardness and soluble orthophosphate, water temperature and pH are known (Krisher 1978).

Magnesium silicate scale is less common in cooling water systems, and forms in two steps: magnesium hydroxide precipitates, then reacts with dissolved and colloidal silica to form a dense, hard-to-remove magnesium silicate scale. Because silica (SiO_2) will not precipitate at concentrations less than 150 $mg{\cdot}L^{-1}$, this silica concentration constitutes a safe upper limit for cooling water systems. Silica solubility decreases with decreasing temperature; hence scale usually forms in the coldest part of the cooling system. Silica solubility also increases with pH, reaching 200 $mg{\cdot}L^{-1}$ at pH 8.5 (Krisher 1978).

Table 5-8 summarizes the water quality guidelines for once-through cooling systems and for water used as makeup. Table 5-9 summarizes water quality guidelines for cooling towers.

5.5 SPECIFIC INDUSTRIAL WATER QUALITY REQUIREMENTS

5.5.1 Steam Electric Power Generation

A steam electric power station is a power plant which uses a steam cycle to produce electrical energy. The heat required to produce steam may be generated by the combustion of fossil fuels, such as coal, oil or gas, or by nuclear fission. Only about one-third of the heat generated is converted to electricity, with most of the remainder being transferred to cooling water. Most

Table 5-8. Water Quality Guidelines for Once-through Cooling and Makeup Water Systems

	Once-through[a]		Makeup for recirculation[a]	
Parameter	Fresh	Brackish[b]	Fresh	Brackish[b]
Silica	<50	<25	<50	<25
Aluminum	NS[c]	NS	<0.1	<0.1
Iron	NS	NS	<0.5	<0.5
Manganese	NS	NS	<0.5	<0.02
Calcium	<200	<420	<50	<420
Bicarbonate	<600	<140	<24	<140
Sulphate	<680	<2700	<200	<2700
Chloride	<600	<19 000	<500	<19 000
Dissolved solids	<1000	<35 000	<500	<35 000
Hardness	<850	<6250	<130	<6250
Alkalinity	<500	<115	<20	<115
pH	5.0-8.3	6.0-8.3	NS	NS
Organic material:				
Methylene blue active substances	NS	NS	<1	<1
Carbon tetrachloride extract	NS[d]	NS[d]	<1	<2
Chemical oxygen demand	<75	<75	<75	<75
Suspended solids	<5000	<2500	<100	<100

[a] Unless otherwise specified all units are mg·L^{-1}.

[b] Brackish water – dissolved solids concentration >1000 mg·L^{-1}.

[c] NS = not specified.

[d] No floating oil.

Source: U.S. EPA 1973.

Table 5-9. Water Quality Guidelines for Cooling Towers

	Numerical limits (mg·L^{-1})		
Parameter	Minimum	Maximum	Comments
Langelier Saturation Index[a]	+0.5	+1.5	Nonchromate programs
Ryzner Stability Index	+6.5	+7.5	Nonchromate programs
pH units	≥6.0	≤8.0	
Calcium (as $CaCO_3$)	>30	<300	Nonchromate program
		<400	Chromate program
Total iron	—	<0.5	
Manganese	—	<0.5	
Copper	—	<0.08	
Aluminum	—	<1	
Sulphide	—	<5	
Silica	—	<150	For pH <7.5
	—	<200	For pH >7.5
$[Ca] \times [SO_4]$	—	<500 000	
Total dissolved solids	—	<2500	
Conductivity (µS·cm^{-1})	—	<4000	
Suspended solids	—	<150	

[a] The limits for the Langelier Saturation Index (an indication of $CaCO_3$ saturation) presume the presence of precipitation inhibitors in nonchromate treatment programs. In the absence of such additives, the limits would be reduced to 0 and 0.5.

Source: Krisher 1978.

steam-generating stations in Canada use once-through cooling systems. Cooling water is pumped from an adjacent water body through the condensers and is discharged back to the water body and not used for recirculation.

Efficient generation of power utilizes high-temperature, high-pressure boilers which have stringent requirements for water quality. These requirements increase with increasing temperature and pressure, and can exceed drinking water quality. These power plants require technically sophisticated water treatment plants to properly treat water for the steam cycle (Krisher 1978).

Most of the water (99.5%) used in steam power plants is for condenser cooling. The water quality requirements are given in Table 5-10. Steam generation, which is approximately 0.4% of the total water use, requires water treated to rigorous standards prior to use in the steam system (Table 5-10).

Water fed to a steam boiler should not (1) form scale or other deposits; (2) cause corrosion in the boiler, feedwater system or

Table 5-10. Water Quality Guidelines for Power Generation Stations

	Concentration ($mg \cdot L^{-1}$)			
	Cooling once-through			
Parameter	Fresh	Brackish[a]	Boiler feedwater (10.35-34.48 MPa)	Misc. uses
Silica	<50	<25	<0.01	—
Aluminum	NS[b]	NS	<0.01	—
Iron	NS	NS	<0.01	<1.0
Manganese	NS	NS	<0.01	—
Calcium	<200	<420	<0.01	—
Magnesium	NS	NS	<0.01	—
Ammonia	NS	NS	<0.07	—
Bicarbonate	<600	<140	<0.5	—
Sulphate	<680	<2700	NS[c]	—
Chloride	<600	<19 000	NS[c]	—
Dissolved solids	<1000	<35 000	<0.5	<1000
Copper	NS	NS	<0.01	—
Hardness	<850	<6250	<0.07	—
Zinc	NS	NS	<0.01	—
Alkalinity (as $CaCO_3$)	<500	<115	<1	—
pH units	5.0-8.3	6.0-8.3	8.8-9.4	5.0-9.0
Organic material:				
Methylene blue active substances	NS	NS	<0.1	<10
Carbon tetrachloride extract	NS[d]	NS[d]	NS	<10
Chemical oxygen demand (COD)	<75	<75	<1.0	—
Dissolved oxygen	—	—	<0.007	—
Suspended solids	<5000	<2500	<0.05	<5

[a] Brackish water – dissolved solids more than 1000 $mg \cdot L^{-1}$.

[b] NS = not specified; the parameter has never been a problem at concentrations encountered.

[c] Controlled by treatment for other constituents.

[d] No floating oil.

Source: Krisher 1978.

condensate return system; (3) foam; and (4) contain silica in concentrations high enough to form turbine blade deposits in high-pressure boilers.

The remaining 0.1% of the water is used for miscellaneous purposes, such as washdown water, seal or bearing cooling water, firefighting system supply, chemical dilution water or ash system makeup water. The water quality requirements are often site-specific, but some generalization is possible. The water must (1) have a pH range of 5-9 so that it is not excessively corrosive; (2) not form scale which could reduce water flow, reduce heat transfer or contribute to corrosion; and (3) have a suspended solids content of less than 5 $mg \cdot L^{-1}$. Such solids can be abrasive and cause failure of pump seals, bearings or valves and controls. The maximum allowable concentration is dependent on the chemical constituents making up the suspended solids.

5.5.2 Iron and Steel Industry

The iron and steel industry includes pig iron production, coke production, steel-making, rolling operations and finishing operations common to steel mills such as tin plating and galvanizing.

For most of the process water used, only a few of the water characteristics have been recognized as causing operational problems. Often, quantity and not quality of the water supply is the prime factor for consideration.

Most integrated steel plants have two or more process water systems. The general plant water supply receives mechanical skimming and straining for control of floating and suspended materials which could harm pumps and possibly internal conditioning. This water is used for coke quenching, slag quenching, gas cleaning and hot-rolling operations. For some of these operations, many mills use recycled water or effluent from another process; hence, the water can be of relatively poorer quality. Water quality guidelines for these process uses are given in Table 5-11.

The other process waters used by the steel industry comprise 2-5% of the total volume. These are often treated by clarification, water softening or demineralization. Clarified water is used mainly in the cold-rolling or reduction mill where surface properties of the product are particularly important. The softened or demineralized water is required for rinse waters following pickling and cleaning operations. The processes requiring the highest-quality water are the coating operations, such as tin plating, galvanizing and organic coating (Table 5-11).

5.5.3 Pulp and Paper Industry

The pulp and paper industry uses a number of manufacturing processes for the production of paperboard and paper products. These include packaging, building materials and paper products ranging from newsprint to coated and un-

Table 5-11. Water Quality Guidelines for the Iron and Steel Industry

	Concentration (mg·L⁻¹)				
			Rinse water		
Parameter	Hot-rolling, quenching, gas cleaning	Cold-rolling	Softened	Demineralized	Steel manufacturing
pH	5.0-9.0	5.0-9.0	6.0-9.0	—	6.8-7.0
Suspended solids	<25	<10	ND[a]	ND	—
Dissolved solids	<1000	<1000	ND	ND	—
Settleable solids	<100	<5.0	ND	ND	—
Dissolved oxygen	(minimum for aerobic conditions)				
Temperature (°C)	<38	<38	<38	<38	<38
Hardness	NS[b,c]	NS[b]	<100	<0.1	<50
Alkalinity	NS[c]	NS[c]	NS[c]	<0.5	—
Sulphate	<200	<200	<200	—	<175
Chloride	<150	<150	<150	ND	<150
Oil	NS	ND	ND	ND	ND
Floating material	NS	ND	ND	ND	ND

[a] ND = not detected.

[b] Controlled by other treatments.

[c] NS = not specified; the parameter has never been a problem at concentrations encountered.

Source: U.S. EPA 1973.

Table 5-12. Effects of Water Quality Parameters on the Pulp and Paper Industry

Parameter	Pitch	Foam	Scale	Corrosion	Deposits	Slime control	Solution stability	Alum use	Rosin sizing	Brightness	Sheet quality	Retention
Hardness	X[a]	X	X	X	X	—	X	X	X	X	—	X
Alkalinity	—	X	X	X	—	—	X	X	X	X	X	X
Sulphates	X	X	X	X	X	—	—	—	X	—	X	X
Chlorides	—	X	—	X	—	—	—	—	—	—	—	—
Silica	—	—	X	—	X	—	X	—	—	—	—	—
Dissolved solids	—	X	—	X	—	—	X	—	X	X	X	X
Carbonates	X	X	X	—	X	X	X	X	X	—	—	X
Colour	—	—	—	—	—	—	—	—	—	X	X	—
Turbidity	—	X	—	X	X	X	—	—	—	X	—	—
pH	X	X	—	X	—	X	X	X	—	—	X	—
Alkyl benzyl sulphonate	—	X	—	—	—	—	X	—	X	—	—	X
Phosphates	—	—	X	—	X	X	—	—	X	—	—	—
Iron	—	—	—	—	X	—	—	—	—	X	X	—
Manganese	—	—	—	—	X	—	—	—	—	X	X	—
Oxygen	—	—	—	X	X	X	—	—	—	—	—	X
Free CO_2	—	—	—	X	X	—	—	—	—	—	—	X
Temperature	—	—	X	X	—	X	—	—	X	—	—	—

[a] X = negative effect.

Source: Fritchie 1978; Frost 1986.

coated writing papers, tissues and others. Water is used for the preparation of cooking and bleaching chemicals, washing, transportation of pulp fibres to the next processing step and formation of the pulp into dry products. Some of the effects that water quality parameters have on various pulp and paper processes are itemized in Table 5-12.

The major problem associated with water quality is low paper brightness, which can be caused by hardness, turbidity, colour and iron (Technical Association of the Pulp and Paper Industry 1957). Table 5-13 presents water quality guidelines for pulp and paper manufacture. The parameters are discussed in more detail below.

5.5.3.1 Hardness

Hard water can cause the formation of insoluble calcium and magnesium resinates during the sizing of paper and paperboard. This interferes with the fibre-covering power of the size. Increased amounts of alum are frequently used to counteract the problem, and sodium aluminate may be added to reduce the total acidity (Nordell 1961).

Hard water can result in the formation of scale in tanks, pipes, deckers, screens, vacuum pumps, beaters, jordans and other equipment. Scale can cause problems in the pulp and papermaking process if it forms on the Fourdrinier or cylinder

Table 5-13. Water Quality Guidelines for the Pulp and Paper Industry

Parameter	Concentration ($mg \cdot L^{-1}$)					
	Fine paper	Ground-wood	Kraft		Chem. pulp & paper	
			Bleached	Unbleached	Bleached	Unbleached
pH	—	6-8	—	—	6-8	6-8
Colour (HU)	<40	<100	<25	<100	<50	<100
Turbidity (NTU)	<10	<20	<40	<100	<10	<20
Calcium	<20	<20	—	—	<20	<20
Magnesium	<12	<12	—	—	<12	<12
Iron	<0.1	<0.1	<0.2	<1.0	<0.1	<1.0
Manganese	<0.3	<0.1	<0.1	<0.5	<0.05	<0.5
Chloride	—	25-75	<200	<200	<200	<200
Silica	<20	<100	<50	<100	<50	<50
Hardness	<100	<100	<100	<100	<100	<100
Alkalinity	40-75	<150	<75	<150	—	—
Dissolved solids	<200	<250	<300	<500	<200	<250
Suspended solids	<10	—	—	—	<10	<10
Temperature (°C)	—	—	—	—	<36	—
CO_2	<10	<10	<10	<10	—	—
Corrosion tendency	NIL	NIL	NIL	NIL	NIL	NIL
Residual chloride	<2.0	—	—	—	—	—

Sources: McKee and Wolf 1963; Eller *et al.* 1970; Walter 1971; Hart 1974; Ontario Ministry of the Environment 1974; Frost 1986.

wire cloth. The life of the cloth is reduced both by the scale and by the corrosive properties of the acids or mechanical means used to remove it (Nordell 1961).

5.5.3.2 Suspended Matter

Suspended matter consists of particles larger than those considered under turbidity. Water for use in the manufacture of pulp and paper should have no suspended matter, because this decreases the brightness of the product, clogs the wires and felts and discolours the pulp or paper. For high-grade paper (e.g. writing bond), the concentration of suspended matter should not exceed 10 $mg \cdot L^{-1}$, whereas 25 $mg \cdot L^{-1}$ should be the upper limit for the other grades (Nordell 1961).

5.5.3.3 Turbidity

Turbidity in water is caused by particles such as clay, silt and microorganisms. A water may be dark yet not turbid; therefore, turbidity and colour should not be confused. Turbidity may adversely affect the brightness and colour of white or tinted papers (Nordell 1961). The recommended upper turbidity limit is dependent on the product (see Table 5-13).

5.5.3.4 Colour

Water of low colour is most desirable for the manufacturing processes, because highly coloured waters may adversely affect both white and dyed papers as well as pulps. Cellulose fibres readily adsorb colouring substances, and the stain may remain in the finished product (Nordell 1961).

Colour in water is usually because of the presence of organic matter and/or iron salts. Organic and iron compounds are difficult to remove from fibres. Problems associated with water having a high organic content can be the result of living organisms, such as slime-forming bacteria, which cause slime spots (Nordell 1961).

5.5.3.5 Iron

Iron in process water causes discolouration of pulp and paper. In surface water, the iron is usually present as colloidally dispersed hydrated ferric oxides, although it may be present in both the ferrous and ferric oxidation states or may be organically bound (Nordell 1961).

In groundwater, iron is usually in solution as ferrous bicarbonate and in soil as insoluble ferric oxide. If water contains appreciable amounts of dissolved organic matter, the iron can be reduced to ferrous oxide which combines with carbonic acid to form soluble ferrous carbonate. If such waters are exposed to air, oxidation may convert the carbonate to insoluble "ferric hydrate". If iron compounds are present in sufficient concentrations, discolouration of pulp and subsequent paper products can result (Nordell 1961).

5.5.3.6 Manganese

Manganese is slowly oxidized to black manganese oxide, which is then deposited in pipes, tanks and other equipment. In bleaching operations, manganese is oxidized to pink permanganate, which similarly discolours fibres (Nordell 1961).

5.5.3.7 Carbon Dioxide

The presence of free carbon dioxide (CO_2) in water (>25 $mg \cdot L^{-1}$) can affect sheet formation and contribute to the corrosive nature of the water. Dissolved oxygen is also corrosive. The combination of high dissolved oxygen and low pH is extremely corrosive. Increasing pH by the addition of alkali decreases the rate of corrosion and builds up a protective film in piping (Nordell 1961).

5.5.3.8 pH

The pH of process water is important in the pulp and paper industry, as water of low alkalinity and high carbon dioxide content is usually corrosive (Nordell 1961).

The economical use of fillers, dyes, sizes or other chemicals may be adversely affected by inadequate control of pH, as many processes and materials are very sensitive to changes in pH. The removal of impurities by adjustment of the hydrogen ion concentration is essential for successful flocculation (Nordell 1961).

5.5.3.9 Other Water Quality Parameters

Chlorides do not usually affect process waters, although excessive concentrations may increase corrosiveness. The chloride concentration is important for some grades of paper, such as for plastic impregnation and dielectric papers.

Sulphates in water may lead to the formation of boiler scale. Silica can aggravate operating problems, as it cements other impurities into a hard boiler scale. In waters which are to be used for boiler purposes, it is usually sufficient to remove the silica, iron and aluminum. Sodium and potassium are usually present in low concentrations in surface fresh waters and groundwaters, and have little effect on this industrial use of water (Nordell 1961).

Hydrogen sulphide is corrosive to metals, and small amounts (0.3 $mg \cdot L^{-1}$) can be corrosive to the wire on Fourdrinier or cylinder machines (Technical Association of the Pulp and Paper Industry 1957).

Odours may be taken up by paper, and should be avoided in paper products for food wrapping or packaging (Technical Association of the Pulp and Paper Industry 1957).

5.5.4 Petroleum Industry

Water is used in the petroleum industry for heat removal, steam generation, processing and sanitation. Water quality guidelines for cooling and steam generation have been discussed in previous sections. The quality requirements for processing are, in most cases, less stringent than those for cooling and steam generation. Limits, however, have been recommended for a few water quality parameters specific to processing operations, and these are given in Table 5-14 (Federal Water Pollution Control Administration 1968).

Table 5-14. Water Quality Guidelines for the Petroleum Industry

Parameter	Concentration $(mg \cdot L^{-1})$[a]
pH units	6.0-9.0
Colour	NS[b]
Calcium	<75
Magnesium	<25
Iron	<1
Bicarbonate	NS
Sulphate	NS
Chloride	<200
Nitrate	NS
Fluoride	NS
Silica	NS
Hardness (as $CaCO_3$)	<350
Dissolved solids	<750
Suspended solids	<10

[a] Unless otherwise indicated.

[b] NS = not specified. The parameter has never been a problem at concentrations encountered.

Sources: Federal Water Pollution Control Administration 1968; Ontario Ministry of the Environment 1974.

5.5.5 Food and Beverage Industry

The food and beverage industry has been divided into 12 categories. Each use has specific water quality requirements so as not to affect the appearance, texture or flavour of foods.

In the food and beverage industry, water is used for a variety of purposes, such as boiler feed, cooling, washing, flushing, processing and general purposes. The requirements for boiler feed and cooling water are much the same as in other industries. The water used for washing, flushing and other general uses should be clear, low in colour, free from iron, manganese and objectionable tastes and odours and of approved bacteriological quality. Also, water for washing operations should preferably be of zero hardness, especially if used with soap or other alkaline detergents.

For process waters, the general specifications are as follows: clear, colourless, free from iron, manganese and objectionable tastes and odours and of approved bacteriological quality, even when the food products are sterilized. Other requirements for process waters vary according to the product. For example, water high in sulphate hardness may be excellent for certain fermentation processes but unusable for canning peas, beans or lentils (Nordell 1961). Water quality guidelines for some of the food industries are described below and summarized in Table 5-15.

5.5.5.1 Carbonated Beverages

Water that is mixed with flavouring materials to produce the final product and used for washing fillers, syrup lines, other product handling equipment and product containers must be of potable quality. Water that is incorporated in the final product must not contain substances that will alter the taste, appearance, or shelf life of the beverage. Because beverages are made from many different syrup bases, the concentration and type of substances that affect taste or other characteristics are not the same for all beverages. Therefore, a single guideline cannot apply to all types of carbonated beverages (U.S. EPA 1973).

For carbonated beverages, ingredient water has more exacting requirements than drinking water. Bottlers often use activated carbon treatment on municipal water to further purify it for beverage use or to remove chlorine compounds. Low-alkalinity water (50-128 $mg \cdot L^{-1}$ as $CaCO_3$) is desirable to minimize neutralization of the beverage acidifying agent. Low organic matter, turbidity, colour and taste are essential. Iron and manganese concentrations must be low to prevent precipitation of the colouring agents. Iron and manganese may also promote the growth of taste- or odour-producing bacteria (Brody 1970).

5.5.5.2 Brewing

Water is used in breweries for brewing, cooling, bottle-washing, keg-washing, pasteurizing and boiler feed.

The brewing water should be clear, colourless, odourless, tasteless, free from iron and manganese and bacteriologically acceptable. Beer production requires water low in alkalinity and high in calcium sulphate to control mash pH (4.6-5.7) for a suitable yeast fermentation. For making light-coloured beer, low bicarbonate and high sulphate contents are desirable. If high in carbonates, the water for such beers may be treated with lime to reduce the bicarbonate hardness. If the water is low in sulphate hardness, calcium sulphate may be added with the lime. This may amount to some 200-250 $mg \cdot L^{-1}$. For dark beers, the bicarbonate content of the brewing water usually requires no reduction (Nordell 1961).

Taste and odour removal is normally carried out to safeguard against any accidental contamination (Nordell 1961).

Iron may discolour beer. Magnesium in excess of 30 $mg \cdot L^{-1}$ imparts a reddish tint and a burning sharp taste. Silica in excess of 50 $mg \cdot L^{-1}$ increases turbidity. Fluoride ion in concentrations greater than 10 $mg \cdot L^{-1}$ inhibits fermentation. Chlorides at concentrations of 20-60 $mg \cdot L^{-1}$ mellow beer (Brody 1970).

Water used in the beverage industry must also be (Sliger 1956):

1. sterile, otherwise bacteria may grow in the beverage and spoil the drink;
2. clear, as appearance is a large factor in the sales appeal of any beverage; in addition, dirt in very small quantities causes foaming, poor carbonation and other bottling difficulties;
3. free of tastes and odours, because these may change the characteristic quality of the beverage;
4. free from organic matter or plant life, because these cause spoilage, rings in the bottles and carbonation difficulties; and
5. uniformly low in alkalinity, because the flavours used in most carbonated beverages are acidic in nature, and alkalinity in the water will react with the acid present, causing loss of flavour and a flat-tasting drink.

Most bottling operations require soft water for bottle-washing. No matter how much care is taken in the washing operation when using hard water, a film of insoluble material is deposited on bottles, leaving them streaked. In addition, hard water consumes larger quantities of the chemicals used for washing.

5.5.5.3 Dairy Operations

Dairy operations use water mostly for cleaning equipment and sometimes for washing products. The water used, there-

Table 5-15. Water Quality Guidelines for the Food and Beverage Industry

	Concentration ($mg \cdot L^{-1}$)							
Parameter	Baking	Brewing	Carbonate beverages	Confectionary	Dairy	Food canning, freezing, dried, frozen fruits, vegetables	Food process (general)	Sugar manufacturing
pH	—	6.5-7.0	<6.9	>7.0	—	6.5-8.5	—	—
Colour (HU)	<10	<5	<10	—	ND	<5	5-10	—
Turbidity (NTU)	<10	<10	1-2	—	—	<5	1-10	—
Taste, odour (units)	low	low	ND[a]	low	ND	ND	low	—
Suspended solids	—	—	—	50-100	<500	<10	—	ND
Dissolved solids	—	<800	<850	50-100	<500	<500	<850	—
Calcium	NS[b,c]	<100	—	—	—	<100	—	<20
Magnesium	—	<30	—	—	—	—	—	<10
Iron	<0.2	0.1-1.0	<0.1	<0.2	0.1-0.3	<0.2	<0.2	<1
Manganese	<0.2[d]	<0.1[d]	<0.05	<0.2[d]	0.03-0.1	<0.2[d]	<0.2	<0.1
Copper	—	—	—	—	ND	—	—	—
Ammonium	—	—	—	—	trace	<0.5	—	—
Bicarbonate	—	ND	—	—	—	—	—	<100
Carbonate	—	<50	<5	—	—	—	—	—
Sulphate	—	<100	<200	—	<60	<250	—	<20
Chloride	—	20-60	<250	<250	<30	<250	—	<20
Nitrate	—	<10	—	—	<20	<10	—	—
Fluoride	—	<1	0.2-1.0	—	—	<1	<1	—
Silica	—	<50	ND	—	—	<50	—	—
Hardness	NS[b]	<70	200-250	—	<180	<250	10-250	<100
Alkalinity	—	<85	50-128	—	—	30-250	30-250	—
Hydrogen sulphide	<0.2	<0.2	<0.2	<0.2	—	—	—	—
Oxygen consumed	—	—	<15	—	—	<1	—	—
Carbon tetrachloride extract	—	—	slight	—	<10	<0.2	—	—
Chloroform extract	—	—	<0.2	—	—	—	—	—
Acidity	—	—	—	—	—	ND	—	—
Phenol	—	ND	ND	—	—	ND	—	ND
Nitrite	—	—	—	—	—	ND	—	—
Organic matter	—	trace	trace	—	—	—	—	trace

[a] ND = not detected.

[b] Some required for yeast action; excess retards fermentation.

[c] NS = not specified.

[d] Total Fe and Mn.

Sources: McKee and Wolf 1963; Eller *et al.* 1970; Hart 1974; Ontario Ministry of the Environment 1974.

fore, should be bacteriologically acceptable and free from chemicals which may leave harmful residues (Hart 1974). Water should be free from copper and low in iron and manganese; these metallic ions catalyze rancidity development. Further, when nonfat dried milk is used as the raw material for cottage cheese production, the water used to reconstitute the dry powder might affect the quality of the finished product. For example, a high sodium content could displace calcium from casein, resulting in a higher uptake of water and formation of a softer curd (Brody 1970).

The water should also be low in hardness to reduce scale formation in bottle-washing machines and other heating equipment. Deposits of scale will enhance bacterial growth which will affect the sterilization process (Funke 1970).

5.5.5.4 Confectionary Production

Confectionary production requires water of low total solids (<100 mg·L^{-1}) for hard candy. The low (1.5%) moisture content of candy accelerates precipitation of salts and clouding of the product. Water with a pH below 7 inverts the sucrose and produces a sticky product. It has been shown that differences in water composition account for failures in duplicating confectionary formulae in different localities (Hart 1974).

5.5.5.5 Sugar Refineries

Sugar refineries require high-quality process water free from dissolved and suspended solids. Hard water forms precipitates which accumulate in the product (Nordell 1961).

5.5.5.6 Canneries

Water for canning should be clear and colourless, free from iron, manganese and objectionable tastes and odours and of acceptable bacteriological quality, even though the finished products are sterilized after being hermetically sealed. In addition, the water used for canning peas, beans and lentils should be free from hardness, as this combines with some of the protein present, making the product tougher and decreasing its grade. For fruits or other acidic products, hardness in the water seems to have little or no effect, with a few exceptions. The oxalates naturally occurring in beets react with the calcium of hard water to form deposits of calcium oxalate, which are especially noticeable on cut beets. A number of other vegetables do not seem to be noticeably affected by water hardness (Nordell 1961).

When softened water of high alkalinity is used in the sterilizing process, the outsides of the cans frequently present a spangled appearance. In such cases, the alkalinity should be lowered to about 50 mg·L^{-1} as $CaCO_3$, either by pretreatment with a cold lime water softener or by softening exchangers to neutralize acidity and yield the desired degree of alkalinity (Nordell 1961).

Fruit and vegetable canners use calcium and magnesium ions for their hardening effect on certain produce. For example, calcium salts are added to tomatoes during canning to prevent structural breakdown and subsequent softening during heat processing (Brody 1970).

5.5.5.7 Bakeries

The water used in bakeries should be clear, colourless, odourless, tasteless, free from iron and manganese and of acceptable bacteriological quality. Some calcium salts are necessary for proper fermentation. These are usually added in yeast food, one of the ingredients of which is calcium sulphate. For cake and cracker baking, softened water has frequently been employed, as it is claimed that it yields a better and more uniform product (Nordell 1961).

5.5.5.8 Distilleries

In general, the water used in distilleries should be clear, colourless, free from iron, manganese, foreign tastes and odours and of acceptable bacteriological quality. Owing to their lower summer temperatures, groundwaters are usually preferred to surface waters, especially for cooling purposes (Nordell 1961).

Some hardness is usually desirable in the water used for mashing, and moderate amounts of bicarbonate hardness are frequently of value as a buffer in maintaining the correct pH during fermentation. If this water is clear and free from undesirable constituents, it is not usually treated. Some distilleries do not treat the water used in the mash coolers even when it is quite hard, but instead rely on periodic removal of scale from the coils (Nordell 1961).

As only new bottles are used in distilleries, rinsing is all that is necessary, and removal of the hardness from this water is not usually required (Nordell 1961).

The water used for deproofing should be free from inorganic suspended matter and also from tastes and odours. This freedom from taste and odour is especially important, for even traces of foreign tastes and odours may seriously impair the quality of the product (Nordell 1961).

5.5.5.9 Meat-packing Plants

Meat packing is a huge industry which covers a great variety of products and by-products. Large quantities of water are used for many different purposes, among which are boiler feed, cooling, washing, flushing, laundering and other cleansing operations, canning and general usage (Nordell 1961).

All water for meat-packing operations should be clear, colourless, odourless, tasteless, free from iron and manganese and of acceptable bacteriological quality (Nordell 1961).

If the water meets the requirements listed above, much of it that is used for flushing, cleansing and other general plant operations is often not treated further. All water for laundering and other alkaline washing operations should be of zero hardness; hence, zeolite water softeners are widely employed. In washing meats for pickling, it is claimed that a better colour is obtained with zeolite-softened water than with hard water (Nordell 1961).

5.5.5.10 Edible-oil Refineries

Edible-oil refineries produce a variety of products, such as salad and cooking oils, hydrogenated oils for shortening and cooking, soaps (laundry, floating, milled and flakes), soap powders and washing powders and various synthetic products, such as synthetic detergents or wetting agents. The process water must meet the general requirements of being clear, colourless, odourless, tasteless, free from iron and manganese and of acceptable bacteriological quality (Nordell 1961). In addition, the water should be free from copper, because this metal is detrimental to oil stability (Ullyot 1986).

5.5.5.11 Starch and Corn Syrup Production

In the production of starch, hard water increases the ash content, and high concentrations of magnesium in the process water may lead to cloudiness in corn syrup. The use of zero-hardness water overcomes these difficulties. Process water must also be free from iron and manganese. It should also meet the requirements of being clear, colourless, odourless, tasteless and of acceptable bacteriological quality (Nordell 1961).

5.5.5.12 Ice Manufacture

Ice is manufactured in a number of the food industries, as well as in plants devoted exclusively to it and in cold-storage plants. A good, saleable ice should be as clear, colourless and free from bubbles, snowy butts and heavy cores as possible. Also, it must not shatter when handled (Nordell 1961).

The water used should be clear, colourless, odourless, tasteless, free from iron and manganese, of acceptable bacteriological quality and have a low mineral salts content. Both calcium carbonate and magnesium carbonate are precipitated on freezing, forming slimy and gritty deposits. Preferably, the bicarbonate hardness of the water should be less than 70 $mg \cdot L^{-1}$. The noncarbonate hardness does not form deposits, but should not be present in excessive amounts as it acts like the sodium salts, as discussed below (Nordell 1961).

Sulphates are considered to be about 1.3 times and sodium bicarbonate 1.6 times as objectionable as chlorides. High concentrations of these salts cause white butts, make heavy cores, retard freezing and, especially for sodium bicarbonate, may cause shattering. Salt concentrations below 343 $mg \cdot L^{-1}$ are usually necessary for a saleable ice, below 257 $mg \cdot L^{-1}$ for a good ice and below 171 $mg \cdot L^{-1}$ for first-quality ice (Nordell 1961).

5.5.6 Chemical and Allied Industries

Chemical industries have several processes which can require water of specific quality. The largest use of water is for cooling and steam generation; other uses include process water, cleaning and transport of materials. Process water can be divided into two categories: (1) water that forms an integral part of the product (e.g. sulphuric acid, nitric acid and hydrochloric acid production); and (2) water that acts as a solvent for an impurity or an effluent gas (Hart 1974).

Water quality requirements for the chemical industry are product-specific. For example, pharmaceuticals and drugs need high-quality water which should be low in colour (<5 Hazen units), low in turbidity (<1 unit) and have a low filterable residue (<10 $mg \cdot L^{-1}$). In addition, water employed in the washing and rinsing of ampoules or containers intended for holding medicinal products require final rinsing with distilled and deionized water. Water used in medicinal preparations intended for ingestion, such as "cough syrup", usually use a "purified water" standard identified in the official monograph of the U.S. Pharmacopeia (1985). The U.S. Pharmacopeia (1985) also lists standards for "Water for Injection", "Bacteriostatic Water for Injection" and "Sterile Water for Injection".

Sodium carbonate and sodium hydroxide manufacture requires a clear soft water to avoid contamination or precipitation of the calcium and magnesium salts. On the other hand, the quality of the water is not critical for chlorine production process water, which is used to dissolve salt (Hart 1974).

In many cases, municipal water can be used for process water without pretreatment. Where doubt exists for special needs, condensate or demineralized water is typically used (Hart 1974). Table 5-16 summarizes water quality guidelines for certain chemical and allied industries.

5.5.7 Textile Industry

The textile industry uses water in a number of processes. Natural fibres (cotton and wool) are spun, teased and woven in the dry state, except for some stiffening of the warp (sizing). The thread is run through the size which is dispersed in a highly concentrated water suspension. After sizing, the natural fibres are generally scoured with soaps, detergents or alkalies to remove the size and natural waxes before bleaching and dyeing. The cloth is bleached before dyeing to obtain a more reproducible colour (Hart 1974).

Scouring requires good-quality water. Cotton is scoured at 80-120°C and pH 12, wool at 45-65°C and pH of 7-10. The bleaching process also varies. Chlorine is used to bleach cotton with the solution adjusted to pH 9. Wool and cotton blends containing synthetic fibres are bleached by hydrogen peroxide at pH 2.5-3.0. The dyeing operations also require high-quality water. Cotton fibres are dyed at pH 7.5-10.0, wool at pH 3.5-6.0 and synthetics at pH 6.5-7.5 (Hart 1974).

Maddison (1971) and Parker (1970) have identified a number of undesirable water quality parameters for textile processing. These include algae, alkalinity, aluminum, calcium, colour, copper, dissolved solids, hardness, hydrogen sulphide, iron, manganese and organic matter.

Colour, iron, manganese, suspended solids and turbidity can all cause textile staining. Iron and manganese can cause black or brown stain when present in concentrations as low as 0.1 $mg \cdot L^{-1}$. Iron concentrations in excess of 1 $mg \cdot L^{-1}$ can also dull dyed shades, yellow bleaches and possibly cause catalytic degradation of cellulose in the hydrogen peroxide bleaching system (Hart 1974).

Hardness, on the other hand, must be removed, because calcium carbonate and magnesium hydroxide would precipitate in the cloth in processes using high pH water (e.g. sizing). Calcium and magnesium also affect many dyestuffs, because a less soluble leuco compound, with little affinity for cellulose, may be formed. For example, Indanthren Blue BC, which is used as a vat dyestuff for cotton, is very sensitive to hard water, and is reportedly affected by a water hardness above 25 $mg \cdot L^{-1}$ (as $CaCO_3$) (Hart 1974).

Table 5-16. Water Quality Guidelines for Chemical and Allied Industries

Parameter	Concentration ($mg \cdot L^{-1}$)								
	Alkalies and chlorine	Organic chemicals	Inorganic chemicals	Clear plastics	Synthetic rubber	Drugs and pharmaceuticals	Soap and detergents	Paints	Fertilizers
pH	NS[a]	6.5-8.7	NS	NS	6.2-8.3	5.0-7.0	NS	NS	NS
Colour units	NS	NS	NS	NS	<20	<5	NS	NS	NS
Turbidity units	—	—	—	<2	—	<1	—	—	—
Taste and odour (threshold)	NS	NS	NS	<2	NS	—	NS	NS	NS
Calcium	<2	<68	NS	NS	<80	[c]	NS	NS	NS
Magnesium	<2	<19	NS	NS	<35	—	NS	NS	NS
Iron	<0.1	<0.1	NS	<0.02	<0.1	—	NS	NS	NS
Manganese	<0.1	<0.1	NS	<0.02[b]	<0.1	—	NS	NS	NS
Bicarbonate	NS	<128	NS	NS	—	—	NS	NS	NS
Sulphate	NS	NS	NS	NS	NS	[c]	NS	NS	NS
Chloride	NS	NS	NS	NS	NS	[c]	NS	NS	NS
Nitrate	NS	NS	NS	NS	NS	—	NS	NS	NS
Silica	NS	NS	NS	NS	NS	—	NS	NS	NS
Hardness (as $CaCO_3$)	low	<250	NS	NS	<350	—	NS	NS	NS
Alkalinity (as $CaCO_3$)	NS	<125	NS	NS	<150	—	NS	NS	NS
Dissolved solids	NS	NS	NS	<200	NS	—	NS	NS	NS
Suspended solids	NS	NS	NS	NS	<5	<10	NS	NS	NS
Dissolved oxygen	NS	NS	NS	NS	NS	—	NS	NS	NS
Chemical oxygen demand	NS	NS	NS	NS	NS	[c]	NS	NS	NS
Biochemical oxygen demand	NS	NS	NS	NS	NS	—	NS	NS	NS

[a] NS = not specified. The water is accepted as received because it has never been a problem at concentrations encountered.

[b] Fe and Mn total.

[c] Test standards established in the official monograph of the U.S. Pharmacopeia (1985) but not translated into minimum acceptable levels (i.e. maximum concentrations).

Sources: Federal Water Pollution Control Administration 1968; Eller *et al.* 1970; Hart 1974.

Table 5-17. Water Quality Guidelines for the Textile Industry

Parameter	Concentration ($mg \cdot L^{-1}$)					
	Cotton, wool, synthetics				Viscose, rayon	
	Sizing suspension	Scouring	Bleaching	Dyeing	Pulp manufacture	Manufacture
Iron	<0.3	<0.1	<0.1	<0.1	<0.05 (Fe + Mn)	ND[a]
Manganese	<0.05	<0.01	<0.01	<0.01	<0.03	ND
Copper	<0.05	<0.01	<0.01	<0.01	<5	—
Dissolved solids	<100	<100	<100	<100	<100	—
Suspended solids	<5	<5	<5	<5	—	—
Hardness (as $CaCO_3$)	<25	<25	<25	<25	<8	<55
pH: Cotton	6.5-10.0	9.0-10.5	2.5-10.5	7.5-10.0	—	—
Synthetics	6.5-10.0	3.0-10.5	NA[b]	6.5-7.5	—	—
Wool	6.5-10.0	3.0-5.0	2.5-5.0	3.5-6.0	—	—
Viscose, rayon	—	—	—	—	—	7.8-8.3
Colour (relative units)	<5	<5	<5	<5	<5	—
Turbidity (NTU)	—	—	—	<15	<5	<0.3
Aluminum	—	—	—	—	<8	—
Silica	—	—	—	—	<25	—
Alkalinity (as $CaCO_3$)	—	—	—	—	50-75	50-75

[a] ND = not detected.

[b] NA = not applicable.

Sources: McKee and Wolf 1963; Hart 1974.

Suspended or colloidal material can affect dyeing operations done under pressure, because the dye liquor is pumped through the yard packages or fabrics which may act as filter media for these materials.

Copper interferes by dulling many dyes and catalytically oxidizing any subsequently applied natural rubber coatings (Simmons 1970). It is also readily adsorbed onto wool (McKee and Wolf 1963). During bleaching, copper can catalyze a reaction with hydrogen peroxide so that holes are formed in the material. Nitrates and nitrites affect wool and silk dyeing. Organic matter, such as humic acid, microorganisms or soil-derived material, interferes with colour hues and causes odours or slimes in the finished product (Hart 1974). Table 5-17 summarizes water quality guidelines for the textile industry.

5.5.8 Tanning and Leather Industry

In the tanning industry, water is utilized in the following processes: preservation, soaking, unhairing, fleshing, scudding, neutralizing, bating, pickling, tanning, retanning, dyeing, fat-liquoring, drying and finishing the hides (Federal Water Pollution Control Administration 1968).

Table 5-18 summarizes the water quality guidelines for the tanning and leather industry. Water should be free from iron and manganese to prevent discolouration and staining. Iron forms dark-coloured precipitates during tanning, ranging from black to dark blue and green according to the origin of the tanning. Any such precipitate reaching the tanning pit causes reduced tanning efficiency and discolours the leather. Water should have low concentrations of free CO_2, bicarbonate, hardness, colour and turbidity. During liming, the presence of bicarbonate and free carbon dioxide may cause the deposition of calcium carbonate precipitates which are dye-resistant. High concentrations of bicarbonates may cause hides to swell (McKee and Wolf 1963). For some processes, such as the finishing of leather, distilled or demineralized water is required.

Table 5-18. Water Quality Guidelines for the Tanning and Leather Industry

	Concentration ($mg \cdot L^{-1}$)		
Parameter	Tanning processes	General finishing processes	Colouring
Alkalinity (as $CaCO_3$)	<130	NS[a]	NS
pH	6.0-8.0	6.0-8.0	6.0-8.0
Hardness (as $CaCO_3$)	<150	NS[b]	ND[c]
Calcium	<60	NS[b]	ND
Chloride	<250	<250	—
Sulphate	<250	<250	—
Iron	<50	<0.3	<0.1
Manganese	—	<0.2	<0.01
Organic materials: Carbon chloroform extract	—	<0.2	ND
Colour (relative units)	<5	<5	<5
Coliform bacteria	NS[d]	NS[d]	—
Turbidity (NTU)	ND	ND	ND

[a] NS = not specified; the water is usually acceptable as received, i.e. it has never been a problem at concentrations encountered.

[b] Lime softened.

[c] ND = not detected.

[d] Should meet drinking water guidelines.

Sources: Hart 1974; Ontario Ministry of the Environment 1974.

5.6 REFERENCES

American Society of Mechanical Engineers. 1979. Consensus on Operating Practices for the Control of Feedwater and Boiler Water Quality in Modern Industrial Boilers. Prepared by Feedwater Quality Task Group for Industrial Boiler Subcommittee of the ASME Research Committee on Water in Thermal Power Systems. Am. Soc. Mech. Eng., New York. 18 pp.

Brody, J. 1970. Ingredient water: analytical requirement. Food Eng. 42: 94-95.

Eller, J., D.I. Ford and E.F. Gloyna. 1970. Water re-use and recycling in industry. J. Am. Water Works Assoc. 62: 149-154.

Federal Water Pollution Control Administration. 1968. Report of the National Technical Advisory Committee on Water Quality Criteria. U.S. Government Printing Office, Washington, D.C. 234 pp.

Fritchie, R.G. (ed.). 1978. Water Supply and Treatment State-of-the-Art. Technical Association of the Pulp and Paper Industry, Atlanta, Georgia. 87 pp.

Frost, M.J. 1986. Personal communication. Canadian Pulp and Paper Association, Montreal, Quebec.

Funke, J.W. 1970. Industrial Water and Effluent Management in the Milk Processing Industry. Natl. Inst. Water Res., Tech. Rep. No. K12, CSIR, Pretoria, South Africa.

Hart, B.T. 1974. A Compilation of Australian Water Quality Criteria. Australian Water Resources Council, Department of Environment and Conservation, Australian Government Publ. Serv., Canberra, Australia. Tech. Pap. No. 7.

Kerr, D.J. 1986. Personal communication. Esso Chemical Canada, Toronto, Ontario.

Krisher, A.S. 1978. Raw water treatment in the CPI. Chem. Eng. (N.Y.) 85: 78-98.

Maddison, P.L. 1971. Water for the world of textiles. Text. J. Austr. 46(7): 22-27, 49-50.

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. State Water Quality Control Board, Resources Agency of California. Publ. No. 3-A. Sacramento, California.

Nordell, E. 1961. Water Treatment for Industrial and Other Uses. 2nd edition. Reinhold Publ. Corp., New York. 598 pp.

Ontario Ministry of the Environment. 1974. Guidelines and Criteria for Water Quality Management in Ontario. Water Resources Branch, Toronto, Ontario.

Parker, C.D. 1970. Water: Its supply, use and disposal. Part 2. Water treatment. Text. J. Austr. 45(12): 55-56.

Simmons, M.W. 1970. Water: Its supply, use and disposal. Water-dyehouse requirements. Text. J. Austr. 45(11): 59-62.

Simon, D.E. and A.W. Fynsk. 1980. Suggested Control Values for Feedwater and Boiler Water Quality in Industrial Boilers. Am. Soc. Mech. Eng. Pap. No. 80-IPC. Pwr-8, New York. 7 pp.

Sliger, H.B. 1956. For better beverages treat your water supplies. Food Eng. 28: 84-86.

Statistics Canada. 1980. Standard Industrial Classification. Supply and Services Canada, Hull. Catalogue No. 12-501E.

Tate, D.M. and D.N. Scharf. 1985. Water Use in Canadian Industry, 1981. Soc. Sci. Ser. No. 19. Water Planning and Management Branch, Inland Waters Directorate, Environment Canada, Ottawa. 39 pp.

Technical Association of the Pulp and Paper Industry. 1957. Water Technology in the Pulp and Paper Industry. TAPPI Monogr. Ser. No. 18. TAPPI, New York. 170 pp.

Ullyot, G. 1986. Personal communication. CPS Foods Ltd., Nipawin, Saskatchewan.

U.S. EPA. 1973. Water Quality Criteria 1972. Environmental Studies Board, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

U.S. Pharmacopeia. 1985. The United States Pharmacopeia. 27th revision. U.S. Pharmacopeial Convention, Inc., Rockville, Maryland.

Walter, J.W. 1971. Water quality requirements for the pulp industry. J. Am. Water Works Assoc. 63: 165-168.

6.0 PARAMETER-SPECIFIC BACKGROUND INFORMATION

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6.0 PARAMETER-SPECIFIC BACKGROUND INFORMATION

6.1 INTRODUCTION

This chapter is a compilation of background information on a broad range of water quality parameters that may be encountered in the Canadian aquatic environment. For each water quality parameter, information is included on uses and production, sources and pathways for entering the aquatic environment, environmental concentrations, and forms and fate in the aquatic environment. The biological effects of water quality parameters are discussed in the preceding guideline chapters on specific water uses.

It must be emphasized that this chapter is not intended to be an exhaustive review of all information published on these water quality parameters. Instead, background information relevant to the development of water quality guidelines has been selected and summarized from existing scientific reviews and some recent primary literature. More detailed information may be found in the references cited for each parameter.

A parameter index appears at the end of the chapter to assist readers in locating information on specific parameters discussed in the chapter.

6.2 INORGANIC PARAMETERS

6.2.1 Acidity, Alkalinity and pH

6.2.1.1 Introduction

Hydrogen ion (H^+) and hydroxide ion (OH^-) are considered to be controlling variables in aqueous systems because they influence both physical-chemical and biological processes in the aquatic environment. The equilibrium between these two ionic species is influenced by reactions with acids and bases introduced into the aqueous system. In a general sense, alkalinity is a measure of the number of hydrogen ions that have reacted over a given pH range during an acid titration, i.e. a measure of water's ability to neutralize acid. Similarly, acidity is the number of hydroxide ions that have reacted over a given pH range during a base titration, i.e. a measure of water's ability to neutralize base. For surface waters, the pH range of interest is typically 4 to 11 (Kramer 1982).

Parameters exerting a significant influence on alkalinity and acidity include nutrients (phosphate, carbonate, ammonia, silicate and sulphide species), metals (iron, manganese and magnesium), organic acids (amino, humic and fulvic acids), gases (carbon dioxide and hydrogen sulphide) and particulates (aluminum, iron and manganese oxides and hydroxides, clay minerals, organic detritus and plankton). Operationally, the acid-neutralizing capacity (ANC) of water is a summation of all the bases that can be titrated with a strong acid to a preselected equivalence point; the ANC pertains to any substance capable of interacting with the hydrogen ion, including dissolved carbonates and hydroxides plus any other protolyte or adsorptive surface or substance. Similarly, the base-neutralizing capacity (BNC) is the equivalent sum of all the acids that can be titrated with a strong base to a predetermined end point (Stumm and Morgan 1981; NRCC 1981; Kramer 1982).

Alkalinity is primarily controlled by carbonate species in water having contact with carbonate minerals (Loewenthal and Marais 1976; Stumm and Morgan 1981). Hence, alkalinity is usually expressed in terms of equivalence to calcium carbonate ($CaCO_3$). Being a relatively weak acid, carbonic acid (H_2CO_3) will dissociate in water and enter into the following equilibria with the dissociation constants (at 25°C) indicated:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad pK_w = 14.0$$
$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \qquad pK_a = 1.47$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad pK_1 = 6.35$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad pK_2 = 10.33$$

The pH of a natural aqueous system containing only carbonate species is a measure of the above acid-base equilibria and is expressed as the negative logarithm of the hydrogen ion activity. In dilute aqueous solution, hydrogen ion activity may be approximated by hydrogen ion concentration. At about pH 6.4, both H_2CO_3 and HCO_3^- concentrations are equivalent. Below pH 6.4, most dissolved carbonate species are in the form of H_2CO_3; above pH 6.4, most are in the form of HCO_3^-. Bicarbonate predominates up to approximately pH 10.3, after which CO_3^{2-} increases in concentration. Hence, in most natural waters containing a carbonate buffering system, the bicarbonate ion predominates (see Section 6.2.20) (Loewenthal and Marais 1976; McNeely *et al.* 1979; Stumm and Morgan 1981; Drever 1982).

6.2.1.2 Sources and Pathways for Entering the Aquatic Environment

Both natural and anthropogenic processes can alter the acid-base balance of a water body. In aquatic systems, pH and alkalinity usually result from the geology and geochemistry of the rocks and soils of the basin. This determines the ANC of the water body, in most cases. Biological activity can influence the variability of pH in aquatic systems. Nutrient cycling and the discharge of industrial effluents to aquatic systems can result in pH fluctuations in natural waterways. The discharge to the atmosphere and subsequent deposition to the aquatic environment of acid-forming substances can also alter natural acid-base balances in water. Such alterations may lead to reduced acid-neutralizing capacity in waters, with subsequent declines in pH (McNeely *et al.* 1979; NRCC 1981).

6.2.1.3 Environmental Concentrations

Alkalinity varies widely in Canadian surface waters, but usually does not exceed 500 $mg \cdot L^{-1}$ as $CaCO_3$. For the majority of Canadian surface waters, alkalinity usually results from the presence of the bicarbonate ion (McNeely *et al.* 1979). There are, however, numerous areas of Canada where surface waters have low alkalinities (<24 $mg \cdot L^{-1}$ as $CaCO_3$); these surface waters are susceptible to alterations in pH (NRCC 1981). Environmental ranges for acidity (total), alkalinity (total) and

Table 6-1. Environmental Ranges for Acidity (Total), Alkalinity (Total) and pH in Canadian Surface Waters

Region	Range[1]	Number of samples	Sampling year(s)
Acidity (total)			
Western	0.5-48.6	15	Prior to 1980
Alkalinity (total)			
Pacific	0.5-162	1 551	1980-1985
Western	1.0-750.0	3 128	1980-1985
Central	ND[2]-210.9	2 464	1980-1985
Atlantic	ND-440	6 679	1980-1985
pH			
Western	4.1-10.2	6 391	1980-1985
Central	2.8-9.6	5 419	1980-1985
Atlantic	2.8-9.2	14 237	1980-1985

[1] Range is in units of mg·L^{-1} for acidity and alkalinity. Detection limit is 0.5 mg·L^{-1} for both acidity (total) and alkalinity (total) (Environment Canada 1979).

[2] ND = not detected.

Source: NAQUADAT 1985.

pH in Canadian surface waters are presented in Table 6-1. A pH range of 6.4-8.9 was reported for 51 sediment samples taken in the Atlantic region prior to 1980 (NAQUADAT 1985).

6.2.1.4 References

Drever, J.I. 1982. The Geochemistry of Natural Waters. Prentice-Hall Inc., Englewood Cliffs, New Jersey. 388 pp.

Environment Canada. 1979. Analytical Methods Manual. Inland Waters Directorate, Ottawa.

Kramer, J.R. 1982. Alkalinity and acidity. *In* Water Analysis. Vol. I. Inorganic Species. Part 1. R.A. Minear and L.H. Keith (eds.). Academic Press, New York. pp. 85-135.

Loewenthal, R.E. and G.V.R. Marais. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Application. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 433 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Alkalinity. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 2.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1981. Acidification in the Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18475. 369 pp.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, New York. 780 pp.

6.2.2 Aluminum

6.2.2.1 Uses and Production

Aluminum is used in alloys and lightweight utensils, castings, airplane parts, construction materials, including exterior siding, sports equipment and electrical conductors (Windholtz *et al.* 1983). Aluminum is also commonly used in dye and paper manufacturing, in tanning industries and as a mordant in printing fabrics. Alum or aluminum sulphate [$KAl(SO_4)_2 \cdot 12H_2O$] is used in water treatment as a flocculating agent for suspended solids, including colloidal materials and microorganisms (U.S. EPA 1973).

Aluminum production in Canada was approximately 1 064 795 t in 1982 or 7.6% of world production. Canada imports all its aluminum ore in the form of bauxite or alumina. Two companies produce primary aluminum metal in Canada: Canadian Reynolds Metals, which operates a 158 760 t·a^{-1} smelter, and the Aluminum Company of Canada Ltd. (Alcan), which operates five smelters for a total of 818 000 t·a^{-1}. In 1982 these two companies were able to maintain production levels at 90% of primary production capacity. Domestic consumption of aluminum for 1982 was estimated at 230 000 t or 0.016% of world consumption (McCutcheon 1984).

6.2.2.2 Sources and Pathways for Entering the Aquatic Environment

Aluminosilicate minerals are abundant in all rock types and most geologic materials, especially clays. Aluminum can be mobilized from soils and sediments by both natural weathering and accelerated acidification processes, resulting in detectable levels in surface waters (Harvey *et al.* 1981).

Anthropogenic sources of aluminum in the aquatic environment include liquid effluents from industries using aluminum in their processing, and the use of alum as a flocculant. Acid mine drainage may also increase aluminum concentrations in surface water (McNeely *et al.* 1979).

Aluminum can also enter the aquatic environment as a result of atmospheric deposition from local and remote sources. Aluminum is one of the principal particulates emitted from the combustion of coal, and aluminum fluoride is emitted from secondary aluminum smelters (Waldbott 1978).

6.2.2.3 Environmental Concentrations

Aluminum is the third most abundant element in the earth's crust; however, it does not occur in its elemental form in nature (U.S. EPA 1973). Most natural surface waters contain less than 1000 μg·L^{-1}, although acidic waters may contain higher concentrations (McNeely *et al.* 1979). Aluminum concentrations from surface water samples taken across Canada are presented in Table 6-2.

6.2.2.4 Forms and Fate in the Aquatic Environment

The fate of aluminum in the aquatic environment is complex and not yet fully elucidated. Generally, the chemistry of aluminum in water is essentially that of aluminum hydroxide, which has several unique features. It is amphoteric; it forms complex ions with other substances in water; and it tends to polymerize. The forms of aluminum in the water column are dictated primarily by pH and the nature of coexisting inorganic and organic ligands (Burrows 1977).

Dissociation of aluminum salts in pure water yields hydrated aluminum ions, generally considered to be in the form $Al(OH)_6^{3+}$; solutions tend to be acidic (pH ≃ 4). Progressive hydrolysis of the aluminum ion yields the univalent ion

Table 6-2. Environmental Concentration Ranges for Aluminum in Canadian Surface Waters

Location	Sample type	pH	Total Al concentration ($\mu g \cdot L^{-1}$)	Reference
Haliburton, Ontario	Background levels	—	2-10	Scheider *et al.* 1978
	26 lakes	5.5-6.0	49	"
Sudbury region, Ontario	5 lakes	4.0-4.6	280-380	"
	2 lakes	5.5	69	"
Smoking Hills, NWT	Temporary pools after rain, June 1977	2.25	70 000	Hutchinson 1980
		2.10	18 000	"
		2.90	4 800	"
		3.00	9 000	"
Various (across Canada)	Stream water	—	50-140	Sorenson *et al.* 1974
Coniston, Ontario	Acid mine drainage	<3.6	<40	Hutchinson 1980
		3.8	1 600	"
	Stream from smelter	7.0	400	"
		7.9	1 000	"
Atlantic region[1]	Surface waters	—	10-1250	NAQUADAT 1985
Quebec[1]	Stream	—	10-1070 (610 samples)	"
Quebec[1]	Stream	—	2 220	"
Quick, B.C.	Upper Bulkley R.	6.3-7.8	5-1700 (16 samples)	Butcher 1985
Chilliwack, B.C.	Fraser R.	6.5-7.1	2 010 (1 sample)	"
British Columbia	St. Mary R.	5.9-8.9	10-9300 (10 samples)	"
Telkwa, B.C.	Telkwa R.	7.1-7.9	<20-5400 (10 samples)	"
Oliver, B.C.	Okanagan R.	7.9-8.5	<20-630 (7 samples)	"
British Columbia	Quinsam R.	5-8.3	<50-70 (35 samples)	"
		5-8.3	6-3300 (27 samples)	"
British Columbia	Flathead R. (at U.S. border)	7.4-8.6	60-280 (4 samples)	"

[1] Detection limit is 50 $\mu g \cdot L^{-1}$ (total).

$Al(OH)_2^+$ and, ultimately, colloidal aluminum hydroxide, $Al(OH)_3$. In alkaline solutions, aluminum hydroxide is amphoteric and is converted to the aluminate anion $Al(OH)_4^-$ (Burrows 1977). Aluminum has a minimum solubility at pH 5.5-6.0; concentrations of total dissolved aluminum increase in the water column at higher and lower pH values. Below pH 4.0, aluminum exists predominantly as the trivalent cation; between pH 4.5 and 6.5, aluminum species include $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$; above pH 6.5, aluminum exists primarily as $Al(OH)_4^-$ (Smith and Hem 1972). Soluble aluminum concentrations in water have been found to increase greatly in lakes having surface water pH values below pH 5-6 (Dickson 1980). For example, in Adirondack lakes and streams, aluminum concentrations varied from 0 to 0.6 $mg \cdot L^{-1}$, corresponding to pH levels ranging from pH 7.2 to 4.2 (Driscoll *et al.* 1980).

Aluminum has a strong tendency to form dimeric, oligomeric and polymeric aluminum hydrates (Smith and Hem 1972). In addition, aluminum is capable of forming numerous complex ions with fluoride, sulphate and organic matter. It has been suggested that in the presence of equimolar or excess fluoride, almost all the aluminum present will be associated with fluoride ions below neutral pH (Lind and Hem 1975). Above about pH 7, hydroxy aluminum complexes predominate. Aluminum sulphate complexes will be present in appreciable concentrations only at low pH (<4.0) and high sulphate levels (>10 $mg \cdot L^{-1}$) (Hem 1968). Numerous organic materials, such as humic acid, fulvic acid, reducing sugars and organic acids, are capable of mobilizing aluminum in the aquatic environment (Beck *et al.* 1974). Levels of soluble aluminum in lake and stream water have been correlated with pH and total organic carbon; aluminum concentrations increased as pH decreased and as organic carbon increased (Driscoll *et al.* 1980). It has been postulated that acid-stressed lakes become clarified as surface water pH declines because of coagulation and precipitation of humic material in the presence of iron and aluminum (Dickson 1980).

6.2.2.5 References

Beck, K.C., J.H. Reuter and E.M. Perdue. 1974. Organic and inorganic geochemistry of some coastal plain rivers in the southeastern United States. Geochim. Cosmochim. Acta 38: 341-364.

Burrows, W.D. 1977. Aquatic aluminum: chemistry, toxicology and environmental prevalence. CRC Crit. Rev. Environ. Control 7: 167-216.

Butcher, G.A. 1985. Personal communication. British Columbia Ministry of Environment, Victoria, British Columbia.

Dickson, W. 1980. Properties of acidified waters. *In* Proc. Int. Conf. Ecological Impact of Acid Precipitation. D. Drablos and A. Tollan (eds.). March 11-14, Sandefjord, Norway. pp. 75-83.

Driscoll, C.T., J.P. Baker, J.J. Bisogni and C.L. Schofield. 1980. Effect of aluminium speciation on fish in dilute acidified waters. Nature (London) 284: 161-164.

Harvey, H.H., R.C. Pierce, P.J. Dillon, J.R. Kramer and D.M. Whelpdale. 1981. Acidification in the Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18475. 369 pp.

Hem, J.D. 1968. Graphical Methods for Studies of Aqueous Aluminum Hydroxide, Fluoride and Sulfate Complexes. U.S. Geol. Surv. Water Supply Pap. No. 1827-B. U.S. Government Printing Office, Washington, D.C.

Hutchinson, T.C. 1980. Effects of acid leaching on cation loss from soils. *In* Effects of Acid Precipitation on Terrestrial Ecosystems. T.C. Hutchinson and M. Havas (eds.). Plenum Press, New York.

Lind, C.J. and J.D. Hem. 1975. Effect of Organic Solutes on Chemical Reactions of Aluminum. U.S. Geol. Surv. Water Supply Pap. No. 1827-G. U.S. Government Printing Office, Washington, D.C.

McCutcheon, W. 1984. Aluminum. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report 32.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Aluminum. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 3.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Scheider, W.A., D.S. Jefferies and P.J. Dillon. 1978. Effects of precipitation on precambrian freshwaters in southern Ontario. J. Great Lakes Res. 5: 45-51.

Smith, R.W. and J.D. Hem. 1972. Effect of Aging on Aluminum Hydroxide Complexes in Dilute Aqueous Solutions. U.S. Geol. Surv. Water Supply Pap. No. 1827-D. U.S. Government Printing Office, Washington, D.C.

Sorenson, J.R.J., I.R. Campbell, L.B. Tepper and R.D. Lingg. 1974. Aluminum in the environment and human health. Environ. Health Perspect. 8: 3-95.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington D.C. EPA-R3-73-033.

Waldbott, G.L. 1978. Health Effects of Environmental Pollutants. The C.V. Mosby Co., St. Louis, Missouri.

Windholtz, M., S. Budavari, R.F. Blumett and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck & Co., Inc., Rahway, New Jersey.

6.2.3 Antimony

6.2.3.1 Uses and Production

Antimony is used in flame retardant materials, paint pigments, ceramic enamels, glass and pottery, plastics, ammunition primers and fireworks. Antimony as a pure metal is used for the production of semiconductors, infrared detectors and diodes. Alloys of antimony are used to manufacture batteries, antifriction materials, printing type and cable sheathing (Lymburner and Knoll 1973; Health and Welfare Canada 1980).

In 1983 and 1984, 385 and 510 t, respectively, of primary antimony were produced in Canada (Energy, Mines and Resources Canada 1985). Since 1981, primary antimony output in Canada has been mostly a by-product of the refining of lead in British Columbia and New Brunswick. Western world mine production was estimated at 24 000 t in 1984, down from the 26 235 t produced in 1983. Canadian consumption of antimony in 1983 was 217 t, but no data on 1984 consumption in Canada were available; it was expected, however, to be slightly lower. Importation of antimony as antimony oxide in 1983 and 1984 was estimated at 1001 t (Bigauskas 1985).

6.2.3.2 Sources and Pathways for Entering the Aquatic Environment

Antimony enters the aquatic environment via natural weathering of rocks and runoff from soils. Antimony occurs in the earth's crust at concentrations of about 0.2-0.5 $mg \cdot kg^{-1}$ (Health and Welfare Canada 1980; U.S. EPA 1979, 1980). Important minerals containing antimony are the native element Sb; stibnite (Sb_2S_3); kermesite (Sb_2S_2O); senarmontite (Sb_2O_3); jamesonite ($2PbS \cdot Sb_2S_3$); and boulangerite ($5PbS \cdot 2Sb_2S_3$). Man-made compounds include stibine (SbH_3), a noxious poisonous gas; the chlorides, $SbCl_3$ and $SbCl_5$; the sulphides, Sb_2S_3 and Sb_2S_5; and the oxides, Sb_2O_3 and Sb_2O_5 (U.S. EPA 1979).

Anthropogenic sources include effluents from mining and manufacturing operations, as well as municipal and industrial discharges (U.S. EPA 1980; Ontario Ministry of the Environment 1981). No data are available on the concentrations of antimony in these discharges.

Antimony is released into the atmosphere from such industrial sources as coal-fired power plants, copper smelters and inorganic chemical plants (Crecelius *et al.* 1974). Antimony is also found in gasolines at concentrations as high as 0.5 $mg \cdot L^{-1}$ (Jungers *et al.* 1975). Antimony may then be transported to the soil and surface water by rain and deposition of dust (Health and Welfare Canada 1980).

6.2.3.3 Environmental Concentrations

Antimony is generally found in trace amounts in surface waters (Ontario Ministry of the Environment 1981). Concentrations of antimony average 1.1 $mg \cdot L^{-1}$ in freshwater streams in the U.S. (U.S. EPA 1980). Ranges of antimony concentrations in Canadian surface waters are presented in Table 6-3. Sampling results for antimony are not recorded in NAQUADAT after 1980 (NAQUADAT 1985).

6.2.3.4 Forms and Fate in the Aquatic Environment

Antimony is commonly found in the +3 and +5 oxidation states. Trivalent antimony complexes with inorganic and organic acids to produce antimonial salts, such as disulphate $(Sb(SO_4)_2)^-$, dioxalate $Sb(C_2O_4)^{2-}$ and the well-known tar-

Table 6-3. Environmental Concentration Ranges for Antimony in Canadian Surface Waters

Region	Concentration range ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<0.01[1]-0.2	49	Prior to 1980
	<0.01	72	Prior to 1980
	<0.001[2]-0.004	19	Prior to 1980
Western	<0.005[1]-1.0	682	Prior to 1980
	<0.004[3]-0.5	11	Prior to 1980
Atlantic	0.001[1]-9.1	320	Prior to 1980

[1] Detection limit is 0.0002 $mg \cdot L^{-1}$ (extractable).

[2] Detection limit is 0.0002 $mg \cdot L^{-1}$ (total).

[3] Detection limit is 0.0002 $mg \cdot L^{-1}$ (dissolved).

Source: NAQUADAT 1985.

trate, $(Sb(OH)C_4H_3O_5)^-$ (Ferguson and Gavis 1972). Examples of complexes in the trivalent state include antimony trioxide, which is not very soluble in water, and antimony trichloride, which is very soluble but which will form insoluble antimony oxychloride. Little is known about the aqueous chemistry of antimony in the +5 oxidation state (Carriker *et al.* 1976).

Under moderately oxidizing conditions, antimony is found as the hydrated trioxide, $Sb_2O_3 \cdot (H_2O)_n$. Unlike arsenic, which forms arsenious acid (H_3AsO_3) under mildly oxidizing conditions, the lower valence acid of antimony is unknown. The antimonites, however, are well-defined salts (Carriker *et al.* 1976).

As a result of the relative stability of the antimonites and antimonates in the redox range typically found in surface waters, most of the antimony introduced into the aquatic environment is probably transported in solution. The extent to which sorption processes reduce the concentrations of antimony in the water column is unknown, although it is known that antimony has an affinity for clay and mineral surfaces. Coprecipitation with hydrous iron, manganese and aluminum may also occur (U.S. EPA 1979). Field surveys have indicated that antimony is bound to sediments, but the degree and extent of binding are unknown (Maxfield *et al.* 1974; Crecelius *et al.* 1975).

In reducing environments, stibine (SbH_3), which is volatile, may be formed. However, it is not stable in aerobic waters and will be readily transformed to the oxide (Sb_2O_3). Photolysis is not considered to be an important process in the removal of antimony from the water column (U.S. EPA 1979).

There are few studies on the bioaccumulation of antimony in the aquatic environment. Bioconcentration factors of 40 and 16 000 were reported for freshwater fish and invertebrates, respectively (Chapman *et al.* 1968). There was no detectable bioconcentration of antimony by bluegill sunfish (*Lepomis macrochirus*) during a 28-d exposure to antimony trioxide (U.S. EPA 1978). The biomethylation of antimony has not been demonstrated; it is, however, thought to occur because the elements surrounding antimony in the periodic table (e.g. Sn, Pb, As, Se, Te) are subject to methylation (Parris and Brinckman 1976).

6.2.3.5 References

Bigauskas, J. 1985. Antimony. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 7.1-7.6.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Crecelius, E.A., C.J. Johnson and G.C. Hofer. 1974. Contamination of soils near a copper smelter by arsenic, antimony and lead. Water Air Soil Pollut. 3: 337-342.

Crecelius, E.A., M.H. Bothner and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9: 325-333.

Energy, Mines and Resources Canada. 1985. Canadian Mineral Production 1983 and 1984. Can. Min. J. 106(2): 26-27.

Health and Welfare Canada. 1980. Antimony. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 147-157.

Jungers, R.H., R.E. Lee, Jr. and D.J. von Lehmden. 1975. The EPA national fuels surveillance network. I. Trace constituents in gasoline and commercial gasoline fuel additives. Environ. Health Perspect. 10: 143-150.

Lymburner, D.B. and H. Knoll. 1973. Antimony, its Production and Use in Canada. Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario.

Maxfield, D., J.M. Rodriguez, M. Buettner, J. Davis, L. Forbes, R. Kovacs, W. Russel, L. Schultz, R. Smith, J. Stanton and C.M. Wai. 1974. Heavy metal pollution in the sediments of the Coeur d'Alene River delta. Environ. Pollut. 7: 1-6.

NAQUADAT. 1985. National Water Quality Data Bank. 1985. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Parris, G.E. and F.E. Brinckman. 1976. Reactions which relate to the environmental mobility of arsenic and antimony II – oxidation of trimethylarsine and trimethylstibine. Environ. Sci. Technol. 10: 1128-1134.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency. Contract No. 68-01-4646.

U.S. EPA. 1979. Antimony. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 5-1 to 5-8.

U.S. EPA. 1980. Ambient Water Quality Criteria for Antimony. Office of Water Regulations and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-020.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

6.2.4 Arsenic

6.2.4.1 Uses and Production

Arsenic is used in pigments, for medicinal purposes, in glassmaking and in alloys with lead and copper. Arsenic compounds (e.g. calcium and lead arsenates, sodium arsenite)

Table 6-4. Importation of Arsenic, Arsenic Oxide and Arsenic Acid into Canada

Compound	Amount (t)	
	1981	1982
Arsenic	86	35
Arsenic oxide	281	251
Arsenic acid	151	31

Source: Statistics Canada 1983.

are also used as pesticides, weed killers, cotton and potato plant defoliants and preservatives. High-purity arsenic is used in manufacturing semiconductors (George 1970; Smith 1973; Demayo *et al.* 1979).

Of the 240 t of arsenic used in Canada in 1974, 67% was used in glass manufacturing, 32% in metal rolling, casting and extruding, and the rest in other chemical industries. In 1971, the production of arsenic in Canada was 34 t. Since then it has declined to almost zero (Statistics Canada 1976a, b, c, d).

Table 6-4 lists imports into Canada in 1981 and 1982 of arsenic and two of its derivatives (Statistics Canada 1983).

6.2.4.2 Sources and Pathways for Entering the Aquatic Environment

Arsenic minerals are widely distributed; the most common are those in which arsenic is combined with sulphur and iron or nickel, e.g. realgar (As_2S_2), mispickel (FeAsS), nickel glance (NiAsS) and niccolite (NiAs) (Demayo *et al.* 1979).

Arsenic is released into the environment by weathering of arsenic-containing rocks and volcanic activity. The global contribution of arsenic by weathering amounts to approximately 40 800 $t{\cdot}a^{-1}$. The amount entering the environment by volcanic activity is probably less (Ferguson and Gavis 1972).

The estimated amount of arsenic released to the global environment annually as a result of human activities is 99 800 t, or about twice that reaching the environment from weathering (Ferguson and Gavis 1972). Most of the arsenic reaching the environment is sorbed by soils and sediment (Carriker *et al.* 1976).

A large part of the world production of arsenic, some 50 000 $t{\cdot}a^{-1}$, reaches rivers, lakes and oceans (Ferguson and Gavis 1972). In addition, arsenic is released to the atmosphere during the processing (smelting and roasting) of sulphide minerals and during the combustion of fossil fuels, especially coal. The presence of arsenic in most pyrites leads to contamination of commercial sulphuric acid, which then causes contamination of other chemicals. For example, certain laundry products contain up to 36 $mg{\cdot}L^{-1}$ of arsenic (Luh *et al.* 1973).

In 1972, stack emissions of arsenic in Canada were estimated at 3700 t. The largest contributor was metallurgical processing in the gold industry (47.5%), followed by primary iron and steel production (25.6%), primary copper and nickel production (16.2%) and primary zinc production (8.8%) (Environment Canada 1976).

6.2.4.3 Environmental Concentrations

Arsenic ranks as the 53rd element in abundance in the earth's crust, with an average concentration of 1.8 $mg{\cdot}kg^{-1}$ (Taylor 1964). Arsenic is more common in the earth's crust than are other common elements such as mercury, iodine, cadmium and silver (Demayo *et al.* 1979).

The arsenic content of fresh waters varies depending on the geochemistry of the region and the proximity of industrial activity and other human activities. In Canada, the dissolved arsenic concentrations in river water samples, collected between 1972 and 1977, ranged from 1 $\mu g{\cdot}L^{-1}$ to approximately 50 $\mu g{\cdot}L^{-1}$, with 90% of the concentrations being below 8 $\mu g{\cdot}L^{-1}$. Lake water samples collected during the same period had arsenic concentrations ranging from 0.5 $\mu g{\cdot}L^{-1}$ to approximately 20 $\mu g{\cdot}L^{-1}$. Some high arsenic concentrations, up to 12.6 $mg{\cdot}L^{-1}$, have been reported in surface waters around the Yellowknife area (NAQUADAT 1977; CPHA 1977).

Between 1980 and 1985, only two regions, Central and Atlantic, had data on total arsenic reported in NAQUADAT. Of the 428 samples taken, only 1 sample (2 $\mu g{\cdot}L^{-1}$) in Quebec was above the detection limit of 1 $\mu g{\cdot}L^{-1}$. The Atlantic region also had values above the detection limit of 5 $\mu g{\cdot}L^{-1}$. The 10 highest values for total arsenic in the Atlantic region ranged from 6.7 to 47 $\mu g{\cdot}L^{-1}$ (NAQUADAT 1985).

6.2.4.4 Forms and Fate in the Aquatic Environment

Arsenic exists in oxidation states of −3, 0, +3 and +5, the two most common being As(III) and As(V). It may form a wide range of compounds with a large number of elements (Lemmo *et al.* 1983). Arsenic as arsenate (AsO_4^{3-}) is the stable form in aerobic water; however, arsenite (AsO_3^{3-}) may be present in surface waters if oxidation to arsenate is incomplete (Demayo *et al.* 1979). Increases in surface water pH, Eh and dissolved oxygen tend to increase the prevalence of higher states of arsenic (NRCC 1978). Arsenic(III) is the predominant form under anaerobic conditions (Carriker *et al.* 1976).

The majority of arsenic in surface water occurs in a soluble form which can be coprecipitated with hydrated iron and aluminum oxides, or adsorbed/chelated by suspended organic matter in water or humic substances in bottom sediments. Arsenic(III) has a strong affinity for sulphur, and it readily adsorbs on and coprecipitates with other metal sulphides (Demayo *et al.* 1979). Arsenic(V) adsorbs on hydrous iron oxides, aluminum hydroxide and clays. Under most conditions, coprecipitation or sorption of arsenic with hydrous iron oxides is probably the predominant process in the removal of dissolved arsenic from the water column (U.S. EPA 1979).

Inorganic forms of arsenic prevail in most natural waters; however, in waters of high organic content, arsenic may be bound to colloidal humic matter (Demayo *et al.* 1979). Both As(III) and As(V) form stable bonds with carbon, resulting in numerous organo-arsenical compounds, some of which are very toxic. An important group of such compounds, from an environmental point of view, is the methylarsines, which are formed by the biological methylation of inorganic arsenic compounds (Wong *et al.* 1977). Dimethylarsinic acid, $(CH_3)_2AsOOH$, is a major and ubiquitous form of arsenic in the environment. It is resistant to oxidation, suggesting that the compound could have a long residence time in surface waters (Demayo *et al.* 1979).

There is no evidence that photolysis is an important removal mechanism of arsenic in the aquatic environment. Volatilization is not considered to be important, except in situations where arsine compounds are present (U.S. EPA 1979).

Arsenic bioaccumulation has been observed in numerous aquatic organisms, including algae, coelenterates, molluscs, crustaceans and fish; the degree of bioaccumulation depends upon the species, age of organism, arsenic concentration and water temperature (NRCC 1978; U.S. EPA 1979; Demayo *et al.* 1979). Bioconcentration factors for aquatic organisms are generally low ($<10^3$) (U.S. EPA 1979). A biological half-life of about 7 d was found in the liver and gut of green sunfish (*Lepomis cyanellus*) (Sorensen 1976). There is no evidence of biomagnification through the food web (Demayo *et al.* 1979). Arsenic may undergo a number of biologically mediated transformations in aquatic environments, including methylation to arsine derivatives (U.S. EPA 1979) and demethylation (Andreae 1979).

6.2.4.5 References

Andreae, M.O. 1979. Arsenic speciation in seawater and interstitial waters: the influence of biological-chemical interactions on the chemistry of trace elements. Limnol. Oceanogr. 24: 440-452.

Carriker, N.E., W.T. Gillespie and P.L. Brezonik. 1976. Boron and Arsenic Studies in Florida Waters. Florida Water Resources Council, Publ. No. 34, Gainesville, Florida. (Cited in Demayo *et al.* 1979.)

CPHA. 1977. Task Force on Arsenic. Final Report. Canadian Public Health Association. Yellowknife, Northwest Territories. (Cited in Demayo *et al.* 1979.)

Demayo, A., M.C. Taylor and S.W. Reeder. 1979. Arsenic. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Environment Canada. 1976. National Inventory of Sources and Emissions of Arsenic (1972). Air Pollution Control Directorate, Environmental Protection Service. Internal Report 75-5.

Ferguson, J.F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6: 1259-1274.

George, J.G. 1970. Arsenic trioxide. *In* Canadian Minerals Yearbook 1969. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 101-105.

Lemmo, N.V., S.D. Faust, T. Belton and R. Tucker. 1983. Assessment of the chemical and biological significance of arsenical compounds in a heavily contaminated watershed. I. The fate and speciation of arsenical compounds in aquatic environments – a literature review. J. Environ. Sci. Health Part A 18: 335-387.

Luh, M.-D., R.A. Baker and D.E. Henley. 1973. Arsenic analysis and toxicity – a review. Sci. Total Environ. 2: 1-12.

NAQUADAT. 1977. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1978. Effects of Arsenic in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15391. 349 pp.

Smith, J.D. 1973. Arsenic, antimony and bismuth. *In* Comprehensive Inorganic Chemistry. Vol. II. J.C. Bailar, Jr., H.J. Emeléus, Sir R. Nyholm and A.F. Trotman-Dickenson (eds.). Pergamon Press, New York. pp. 547-684.

Sorensen, E.M.B. 1976. Thermal effects on the accumulation of arsenic in green sunfish, *Lepomis cyanellus*. Arch. Environ. Contam. Toxicol. 4: 8-17.

Statistics Canada. 1976a. Glass and Glass Products Manufacturers 1974. Catalogue No. 44-207.

Statistics Canada. 1976b. Metal Rolling, Casting and Extruding 1974. Catalogue No. 41-215.

Statistics Canada. 1976c. Miscellaneous Chemical Industries 1974. Catalogue No. 46-216.

Statistics Canada. 1976d. Smelting and Refining 1974. Catalogue No. 41-214.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285.

U.S. EPA. 1979. Arsenic. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. 1. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 6-1 to 6-17.

Wong, P.T.S., Y.K. Chan, L. Luxon and G.A. Bengert. 1977. Methylation of arsenic in the aquatic environment. Trace Subst. Environ. Health 9: 100-106.

6.2.5 Asbestos

6.2.5.1 Uses and Production

Asbestos is the common name given to fibrous mineral compounds (silicates) belonging to the serpentine (chrysotile) and amphibole (actinolite, amosite, anthophyllite, crocidolite, tremolite) mineral groups (Shugar 1979; Health and Welfare Canada 1980). The fire-resistant properties of asbestos make it a valuable component in fireproofing materials. The tensile strength and flexibility of some types of asbestos make them suitable for weaving heat-resistant textiles for fireproof curtains, garments and gloves. Building materials using asbestos include insulation against heat and noise, floor and ceiling tiles, asphalt felts, coating and patching compounds, sheets and pipes. Asbestos is also used in brake linings and clutch facings because of its friction-resistant qualities. Other uses include electrical insulation and certain paper products (Shugar 1979; Health and Welfare Canada 1980; U.S. EPA 1980).

In 1982, Canadian asbestos production was approximately 1.12×10^6 t, or about 24.6% of world production, second after the U.S.S.R. In 1982, 85-90% of Canadian asbestos production came from Quebec. Canada's consumption was only 1.2% of world production. Ninety percent of Canadian asbestos production is chrysotile, and the remaining production consists of 6% crocidolite, 3% amosite and <1% of other types of asbestos (Vagt 1984). Chrysotile is the most widely used type of asbestos, accounting for more than 95% of world production (Speil 1974; Shugar 1979). The major users of asbestos are the U.S.A. and U.S.S.R. (Vagt 1984).

6.2.5.2 Sources and Pathways for Entering the Aquatic Environment

Asbestos is derived from rock with a high content of ferromagnesium silicates. In addition to mineral ore, asbestos fibres occur in soil, water and air (Shugar 1979). Canada has the largest asbestos reserves, an estimated 130×10^6 t, based on 1975 known world deposits (Lamarche 1975).

Asbestos fibres enter the aquatic environment by natural weathering erosion processes and from industrial sources (IJC 1977; Shugar 1979). Of the estimated 243 527 t of asbestos discharged to the environment in the United States (based on 1975 data), 98.3% was discharged on land, 1.5% to air and 0.2% directly to water. Solid waste disposal by consumers was the single largest contributor to total discharge (U.S. EPA 1980). Industrial sources include the dumping of certain mine tailings into aquatic systems and runoff of process and air scrubber water into lakes and streams (Shugar 1979).

Asbestos fibres can be introduced directly into water supplies from asbestos-cement pipes (Shugar 1979; Health and Welfare Canada 1980). This release is determined by the "aggressiveness" of the water supply, which is an index based on pH, total alkalinity and calcium hardness (Kramer and Murdock 1974; Buelow *et al.* 1980).

Atmospheric pollution also contributes to the presence of asbestos fibres in natural waters. This may result from fallout into aquatic systems, or from fallout onto land and subsequent runoff to aquatic environments. In 1974, asbestos emissions to the atmosphere from Canadian sources were estimated to be 7140 t (Gagan 1977). Sources included asbestos mining, asbestos milling, manufacturing and utilization of asbestos products (MacLaren, J.F., Ltd. 1973).

6.2.5.3 Environmental Concentrations

Asbestos levels in rivers and lakes vary considerably, depending on the proximity of the water bodies to industrial sources. Background concentrations are considered to be about 10^6 fibres per litre (Kramer and Murdock 1974), with a reported range of $(<1\text{-}10) \times 10^6$ fibres per litre (Cunningham and Pontefract 1971; IJC 1974). It has been suggested that the natural background concentration of asbestos in the Great Lakes, prior to human influence, was approximately 10^5 fibres per litre (Cook 1977). Sampling results for asbestos are not reported in NAQUADAT.

6.2.5.4 Forms and Fate in the Aquatic Environment

Asbestos is composed of silicon, oxygen, hydrogen and one or more metal cations, including sodium, magnesium, calcium and iron. Unlike other asbestos minerals, chrysotile fibres have a positive charge in aqueous systems. They will attract, or be attracted to, most dispersed materials. The highly reactive surface of asbestos causes many surface reactions, ranging from simple adsorption to true chemical reaction (U.S. EPA 1980).

The fate of asbestos fibres in aquatic environments is believed to be affected by sedimentation, resuspension and migration. However, the residence time of asbestos in water is unknown (IJC 1974).

Experimental studies suggest that chrysotile is slowly solubilized in water under conditions of continuous extraction (Hostetler and Christ 1968; Chowdhury 1975). It has also been suggested that the presence of trace metals will produce a suspension of chrysotile in water which will persist until sufficient magnesium is leached from the chrysotile structure (U.S. EPA 1979). Studies in Lake Superior have indicated that, although asbestos fibres can travel significant distances in the water column, they can be coagulated and sedimented (Kramer 1976).

It appears that sediment does not have an adsorptive affinity for solid materials, such as asbestos, normally encountered in natural waters. However, numerous inorganic and organic materials may be adsorbed to asbestos. More than 60 compounds have been observed to be adsorbed to asbestos (Hilborn *et al.* 1974). Commercially milled Canadian chrysotile contained 5-200 $mg \cdot kg^{-1}$ organic matter, mostly as *n*-alkanes, with little, if any, polycyclic aromatic hydrocarbons (Gibbs and Hui 1971).

There is little information on the accumulation of asbestos fibres in the tissues of aquatic organisms. Fish living in water with high asbestos fibre concentrations do not accumulate levels of asbestos which could be a threat to human health (Shugar 1979). No evidence was found regarding the bioaccumulation of asbestos in aquatic organisms (U.S. EPA 1979).

6.2.5.5 References

Buelow, R.W., J.R. Millette, E.F. McFarren and J.M. Symons. 1980. The behavior of asbestos-cement pipe under various water quality conditions: a progress report. J. Am. Water Works Assoc. 72: 91-102.

Chowdhury, S. 1975. Kinetics of leaching of asbestos minerals at body temperatures. J. Appl. Chem. Biotechnol. 25: 347-353.

Cook, P.M. 1977. Personal communication. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota. (Cited in Shugar 1979.)

Cunningham, H.M. and R.D. Pontefract. 1971. Asbestos fibres in beverages and drinking water. Nature (London) 232: 332-333.

Gagan, E.W. 1977. Air Pollution Emissions and Control Technology. Asbestos Mining and Milling Industry. Environmental Protection Service, Environment Canada. Rep. No. EPS 3-AP-76-6. 54 pp.

Gibbs, G.W. and H.Y. Hui. 1971. The organic content of Canadian chrysotile. Am. Ind. Hyg. Assoc. J. 32: 519-528.

Health and Welfare Canada. 1980. Asbestos. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 179-194.

Hilborn, J., R.S. Thomas and R.C. Lao. 1974. The organic content of international reference samples of asbestos. Sci. Total Environ. 3: 129-140.

Hostetler, P.B. and C.L. Christ. 1968. Studies in the system $MgO\text{-}SiO_2\text{-}CO_2\text{-}H_2O(l)$: the activity product constant of chrysotile. Geochim. Cosmochim. Acta 32: 485-497.

IJC. 1974. Asbestos in the Great Lakes with Emphasis on Lake Superior. International Joint Commission, Windsor, Ontario.

IJC. 1977. Asbestos. *In* New and Revised Great Lakes Water Quality Objectives. Vol. II. Report to the Governments of the United States and Canada, International Joint Commission, Windsor, Ontario. pp. 142-143.

Kramer, J.R. 1976. Fibrous cummingtonite in Lake Superior. Can. Mineral. 14: 91-98.

Kramer, J.R. and O. Murdock. 1974. Asbestos research at McMaster University. Can. Res. Dev. 7(6): 31.

Lamarche, R.Y. 1975. Third International Conference on Physics and Chemistry of Asbestos Minerals. Geosci. Can. 2: 200-204.

MacLaren, J.F., Ltd. 1973. National Inventory of Sources and Emissions of Asbestos (1970). Air Pollution Control Directorate, Environmental Protection Service, Environment Canada. Rep. No. APCD 73-4. 46 pp.

Shugar, S. 1979. Effects of Asbestos in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16452. 185 pp.

Speil, S. 1974. Chrysotile in water. Environ. Health Perspect. 9: 161-163.

U.S. EPA. 1979. Asbestos. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 7-1 to 7-17.

U.S. EPA. 1980. Ambient Water Quality Criteria for Asbestos. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-002.

Vagt, G.O. 1984. Asbestos. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report 32.

6.2.6 Barium

6.2.6.1 Uses and Production

Barium is used in the manufacture of metal alloys, paints, pigments, paper, soap, rubber, linoleum, cement and various other products (Ontario Ministry of the Environment 1981). Barium is also used in fabric printing and dyeing, ceramic glazes and enamels, and in flares, explosives and lubricating oils. Barium compounds are used in oil drilling muds and in the processing of diesel fuels. Barium sulphate acts as a contrast material in radiological diagnoses and is also used in cosmetics. Barium carbonate is used in the production of optical glasses, in the case-hardening of steel and as a rat poison (Pigeon and Preisman 1967; McNeely *et al.* 1979; Health and Welfare Canada 1980; Ontario Ministry of the Environment 1981).

Barium occurs chiefly as the mineral barite ($BaSO_4$). In 1984, 46 884 t of barite were produced in Canada; in 1983, 28 t were produced. World production was ~791 000 t of barite in 1983 (Vagt 1985). Importation in 1983 and 1984 was estimated at 29 952 and 16 311 t, respectively (Statistics Canada 1984). Imports of witherite or barium carbonate ($BaCO_3$), one of the most important barium compounds derived from barite, amounted to 3699 t in 1983 (Statistics Canada 1984; Vagt 1985). In 1983, 7616 t of barium sulphate (refined) and 29 951 t of barium sulphate (natural unrefined) were imported into Canada. In 1983, 4 t of barium oxide were imported into Canada (Vagt 1985).

6.2.6.2 Sources and Pathways for Entering the Aquatic Environment

The weathering of barite ($BaSO_4$) and witherite ($BaCO_3$), as well as other barium minerals in igneous rocks, releases barium to surface waters. Barium is found in sedimentary formations with feldspar, where it replaces potassium, and in freshwater and deep-sea manganese oxide concretions (Cronan and Thomas 1972; Friberg *et al.* 1979). Although barium carbonate and sulphate are insoluble, most of the other barium salts are soluble (McNeely *et al.* 1979). Barium salts, such as barium acetate, nitrate and chloride, are used for fabric printing and dyeing, and the manufacture of paints, explosives, lubricating oils, paper and synthetic rubber. These activities may discharge barium into receiving waters. Since barite is used as drilling mud, barium may also be present in drilling wastewater (McNeely *et al.* 1979). Concentrations of barium compounds in these industrial effluents are not available.

Table 6-5. Environmental Concentration Ranges for Total Barium in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	<0.1[1]	19	Prior to 1980
Western	ND[1,2]-0.23	162	Prior to 1980
	0.001[3]-2.2	1761	1980-1985
Central	0.05[1]-0.07	9	1984
Atlantic	0.02[1]-1.0	9	Prior to 1980

[1] Detection limit is 0.02 mg·L^{-1} (total).

[2] ND = not detected.

[3] Detection limit is 0.1 μg·L^{-1}.

Source: NAQUADAT 1985.

6.2.6.3 Environmental Concentrations

Although barium is a common element in the earth's crust, only trace levels are normally found in aquatic systems. Concentrations of barium above 1 mg·L^{-1} are not usually found. As a result, very few surface water analyses for barium are reported in Canada (McNeely *et al.* 1979). Environmental concentrations for barium (total) in Canadian surface waters are presented in Table 6-5.

Barium concentrations in surface water are sometimes as high as 0.340 mg·L^{-1}. A maximum barium concentration of 1.6 mg·L^{-1} (extractable) was measured in one sample from the Flathead River, B.C., in 1976 (Buchanan 1985). Concentrations of 0.035 mg·L^{-1} have been found in the St. Lawrence River and in Lake Erie (Tong *et al.* 1972). Groundwater in British Columbia at a proposed coal mine site contained dissolved barium at an average concentration of 7.3 mg·L^{-1} (range of 1.2-10.8 mg·L^{-1}) (Buchanan 1985). Seawater usually contains approximately 0.02 mg·L^{-1} barium (McNeely *et al.* 1979).

6.2.6.4 Forms and Fate in the Aquatic Environment

Barium occurs in oxidation states of 0 and +2; in addition, some organometallic compounds containing barium are known, but they tend to readily dissociate in aqueous systems (Venugopal and Luckey 1978; Cotton and Wilkinson 1980). Barium is usually found in only trace amounts in natural surface waters because it is readily removed from the water column by precipitation or sorption and sedimentation. Although the acetate, nitrate and halide salts of barium are soluble in water, the carbonate, sulphate, chromate, fluoride, oxalate and phosphate salts are quite insoluble (Hem 1970). The presence of sulphate and carbonate ions limits the concentration of barium in water by causing it to precipitate. The solubility products of barium sulphate and carbonate are 1.5×10^{-6} and 1.6×10^{-6}, respectively (Butler 1964), indicating that very little barium would occur in solution. As a result, the barium concentrations of sediments (90-2300 mg·kg^{-1}) are higher than concentrations reported in fresh water (<3-150 μg·L^{-1}) (Bowen 1979).

Barium accumulates in some marine biota. Concentration factors of 17 000 in phytoplankton, 900 in zooplankton and 8 in fish muscle have been reported (Lowman *et al.* 1971). There is no indication of biomethylation (Venugopal and Luckey 1978).

6.2.6.5 References

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Buchanan, R.J. 1985. Personal communication. Water Management Branch, British Columbia Ministry of Environment, Victoria, British Columbia.

Butler, J.N. 1964. Ionic Equilibria: A Mathematical Approach. Addison-Wesley, Reading, Massachusetts. 547 pp.

Cotton, P.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Cronan, D.S. and R.L. Thomas. 1972. Geochemistry of ferromanganese oxide concretions and associated deposits in Lake Ontario. Geol. Soc. Am. Bull. 83: 1493-1501.

Friberg, L., G.F. Nordberg and V.B. Vouk (eds.). 1979. Barium. *In* Handbook on the Toxicology of Metals. Elsevier/North Holland Biomedical Press, New York. pp. 321-328.

Health and Welfare Canada. 1980. Barium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 195-203.

Hem, J.D. 1970. Barium. *In* Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geol. Surv. Water Supply Pap. 1473. Washington, D.C. p. 197.

Lowman, F.G., T.R. Rice and F.A. Richards. 1971. Accumulation and redistribution of radionuclides by marine organisms. *In* Radioactivity in the Marine Environment. National Academy of Sciences, Washington, D.C. pp. 161-199.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Barium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 7.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Pigeon, L.M. and L. Preisman. 1967. Barium and barium compounds. *In* Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 3. 2nd edition. p. 77.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Tong, S.C., W.H. Gutenmann, D.J. Lisk, G.E. Burdick and E.J. Harris. 1972. Trace metals in New York State fish. N.Y. Fish Game J. 19: 123. (Cited in Health and Welfare Canada 1980.)

Vagt, G.O. 1985. Barite and celestite. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 10.1-10.7.

Venugopal, B. and T.D. Luckey. 1978. Metal Toxicity in Mammals. Vol. 2. Plenum Press, New York. pp. 63-67.

6.2.7 Beryllium

6.2.7.1 Uses and Production

Beryllium is used in the production of light alloys, copper and brass, in the production of X-ray tubes and neon sign electrodes, and as a catalyst in the manufacture of organic chemicals. Beryllium has also been used experimentally in rocket and aircraft fuels and nuclear reactors (McNeely *et al.* 1979).

Beryllium is produced commercially from two minerals, beryl and bertrandite. Beryl has been mined in Canada, but there has been no production in recent years. Bertrandite, which has not been mined in Canada, has become the most important source of beryllium metal in the western world. World beryllium production, which occurs in the U.S.A. and U.S.S.R. almost exclusively, has been estimated at 200 and 250 t, respectively, in 1984. In 1983, the U.S.A. and U.S.S.R. produced 186 and 235 t of beryllium, respectively (Bokovay 1985). Importation into Canada of beryllium metal and beryllium alloys is presented in Table 6-6.

Table 6-6. Importation of Beryllium Metal and Beryllium Alloys into Canada

	Amount (t)	
Compound	1981	1982
Beryllium primary forms and fabricated materials	4501	2192
Beryllium alloys primary forms and fabricated materials	4411	4522

Source: Statistics Canada 1983.

6.2.7.2 Sources and Pathways for Entering the Aquatic Environment

Beryllium is found chiefly as the minerals beryl ($Be_3Al_2Si_6O_{18}$), bromellite (BeO), chrysoberyl ($BeAl_2O_4$) and beryllonite ($NaBePO_4$). In common crystalline rocks, the element is enriched in the feldspar minerals relative to ferromagnesium minerals, and apparently replaces the silicon ion; 85-98% of the total crustal beryllium may be bound in feldspar structures (Beus 1966). Beryllium enters natural waters through the weathering process, atmospheric fallout and discharges from industrial and municipal operations (Tepper 1972).

The major source of beryllium in the environment is the combustion of fossil fuels (Tepper 1972). It was assessed that if 500×10^6 t of Illinois and Appalachian coal with a beryllium concentration of 2.5 mg·kg^{-1} were burned annually, the potential release of beryllium from this source in the United States would approximate 1260 t, or five times the world production. Beryllium concentrations in air ranged from 1 to 2 ng·m^{-3} in urban areas and averaged 0.13 ng·m^{-3} in rural areas (Tabor and Warren 1958; U.S. Department of Health, Education and Welfare 1968).

6.2.7.3 Environmental Concentrations

Beryllium is found in the earth's crust at an average concentration of 2.5 mg·kg^{-1} (Weast 1977). The average concentration of beryllium in most surface fresh waters has been estimated to be less than 1 μg·L^{-1}. Dissolved beryllium concentrations in the Western region were found to be <5 μg·L^{-1} (detection limit 1 μg·L^{-1}) for 120 samples taken prior to 1980. The Pacific and Western regions recorded extractable beryllium concentrations prior to 1980 below 5 μg·L^{-1} for 17 samples and below 10 μg·L^{-1} for 680 samples, respectively (NAQUADAT 1985). In seawater, concentrations of beryllium are approximately 0.6 ng·L^{-1} (McNeely *et al.* 1979).

6.2.7.4 Forms and Fate in the Aquatic Environment

Except for its metallic form, beryllium exists primarily in the +2 oxidation state. Most common beryllium compounds are readily soluble in water (U.S. EPA 1980). Beryllium chloride and nitrate are very soluble in water, and beryllium sulphate is moderately soluble, whereas beryllium carbonates and hydroxides are practically insoluble (U.S. EPA 1976; McNeely *et al.* 1979).

At acidic pH, beryllium behaves as a cation; at pH values greater than 8, it forms anionic complexes (Drury *et al.* 1978). Beryllium has a complicated coordination chemistry, and can form complexes, oxycarboxylates and chelates with a variety of materials (Bertin and Thomas 1971). In aqueous solution, beryllium does not exist as actual Be(II) ions but as hydrated complexes, in particular beryllium hydroxide ($Be(OH)_2$). During the process of weathering, beryllium concentrates as a hydrolysate in the clay mineral fraction and does not enter solution to any appreciable extent (McNeely *et al.* 1979).

In most aquatic environments, beryllium is present in particulate rather than dissolved form, primarily because of the insolubility of beryllium oxides. Although little information is available on sorption of beryllium, surveys have shown that it is concentrated in sediments relative to the water column (Meehan and Smythe 1967; U.S. EPA 1980). Bioconcentration factors range from 19 for bluegill sunfish (*Lepomis macroch*[illegible] exposed to beryllium for 21 d (U.S. EPA 1978) to 100 for freshwater plants, invertebrates and fish (Chapman *et al.* 1968). No evidence of biomagnification in freshwater ecosystems has been found (Cowgill 1973).

6.2.7.5 References

Bertin, F. and G. Thomas. 1971. Sur la chimi de coordination du béryllium. Bull. Soc. Chim. Fr. 10: 3467-3498. (Cited in U.S. EPA 1979.)

Beus, A.A. 1966. Distribution of beryllium in granites. Geochemistry (USSR) 5: 432-437. (Cited in U.S. EPA 1980.)

Bokovay, G. 1985. Beryllium. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 12.1-12.5.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Cowgill, U.M. 1973. Biogeochemical cycles for the chemical elements in *Nymphaea odorata* Ait. and the aphid *Rhopalosiphum nymphaeae* (L.) living in Linsley Pond. Sci. Total Environ. 2: 259-303.

Drury, J.S., C.R. Shriver, E.B. Lewis, L.E. Towill and A.S. Hammons. 1978. Reviews of the Environmental Effects of Pollutants: VI. Beryllium. Oak Ridge National Laboratory, Oak Ridge, Tennessee. PB 290-966. pp. 8-38. (Cited in U.S. EPA 1979.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Beryllium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 7-8.

Meehan, W.R. and L.E. Smythe. 1967. Occurrence of beryllium as a trace element in environmental materials. Environ. Sci. Technol. 1: 839-844.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tabor, E.C. and W.V. Warren. 1958. Distribution of certain metals in the atmosphere of some American cities. Arch. Ind. Health 17: 145. (Cited in U.S. EPA 1980.)

Tepper, L.B. 1972. Beryllium. *In* Metallic Contaminants and Human Health. D.H.K. Lee (ed.). Academic Press, New York. p. 127. (Cited in U.S. EPA 1980.)

U.S. Department of Health, Education and Welfare. 1968. National Air Sampling Network, Air Quality Data. Public Health Service, Durham, North Carolina. (Cited in U.S. EPA 1980.)

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 21-24.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency. Contract No. 68-01-4646.

U.S. EPA. 1979. Beryllium. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 8-1 to 8-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Beryllium. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-024.

Weast, R.C. (ed.) 1977. Handbook of Chemistry and Physics. 58th edition. CRC Press, Cleveland, Ohio. 2398 pp.

6.2.8 Boron

6.2.8.1 Uses and Production

Boron is used in fire retardants; in the manufacture of borosilicate glass; as a component of enamels, and antioxidants for soldering; and in the photographic, cosmetic, leather, textile, paint and wood-processing industries (U.S. EPA 1976; McNeely *et al.* 1979; Health and Welfare Canada 1980). It is also used in the preparation of disinfectants and drugs. Boron hydrides can form highly flammable mixtures with oxidizing compounds, and are used in some synthetic rocket fuels (Health and Welfare Canada 1980).

Borax ($Na_2B_4O_7 \cdot 10H_2O$), a major boron compound, is used as a cleaning compound, and may occur in domestic and/or industrial effluents (Health and Welfare Canada 1980). Elemental boron is used in metallurgy to harden metals (McNeely *et al.* 1979), in nuclear reactors for neutron absorption (U.S. EPA 1976) and in agriculture, in very small amounts, to improve crop yields (McNeely *et al.* 1979).

Boron and its compounds are not manufactured in Canada (Chemical Information Services, Ltd. 1980). Importation of borax and boric acid was reported as 51 600 t in 1978 and 2000 t in 1976, respectively (CORPUS Information Services 1978, 1980). Boron trifluoride import values for 1981, 1982 and 1983 were reported as 8, 7 and 28 t, respectively. Boron nitride was imported in 1981, 1982 and 1983 in the reported amounts 15, 77 and 63 t, respectively (Statistics Canada 1983).

6.2.8.2 Sources and Pathways for Entering the Aquatic Environment

More than 80 minerals which contain boron are known, of which the most common is tourmaline, a complex silicate mineral present in igneous rocks (McNeely *et al.* 1979; Health and Welfare Canada 1980) and some sedimentary rocks. The weathering of both igneous and sedimentary rocks releases boron, which is then transported in solution. Soil leaching may also add boron to waters (McNeely *et al.* 1979). Volcanic action can contribute boron to the environment by releasing boric acid and boron trifluoride (Health and Welfare Canada 1980).

Boron has a wide variety of industrial uses and, therefore, many potential pathways for entering the aquatic environment. Boron may be found in domestic sewage as a result of its use as a water softener (borax) and a mild antiseptic (boracic). Boron may also find its way into surface waters through agricultural runoff (pesticide application) and in areas where boron is used to improve crop yields (McNeely *et al.* 1979; Health and Welfare Canada 1980). No data are available on amounts of boron released from anthropogenic sources.

6.2.8.3 Environmental Concentrations

Boron concentrations in surface waters average 0.1 mg·L^{-1} (McNeely *et al.* 1979); however, concentrations up to 6.5 mg·L^{-1} (U.S. surface waters) have been reported (Durfor and Becker 1962). Over 90% of the water quality stations surveyed across Canada in 1976 had median boron values below 0.5 mg·L^{-1}, with provincial median values ranging from 0.01 mg·L^{-1} for British Columbia to 0.15 mg·L^{-1} for Manitoba and Saskatchewan (NAQUADAT 1976). Lake water samples from New Brunswick, Ontario and Saskatchewan contained between 0.005 and 0.7 mg·L^{-1} (Afghan *et al.* 1972). Canadian boron concentrations, obtained from NAQUADAT (1985), are presented in Table 6-7. Snow samples from the Ottawa area contained boron at 0.001-0.012 mg·L^{-1} (Afghan *et al.* 1972). Hot springs and brines have been found to contain boron concentrations as high as 48 mg·L^{-1} (McNeely *et al.* 1979).

Table 6-7. Environmental Concentration Ranges for Dissolved Boron in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	<0.01-2.00	418	Prior to 1980
Western	0.01-0.59	166	Prior to 1980
Central	<0.01-3.69	324	Prior to 1980
Atlantic	<0.01-2.30	417	Prior to 1980

[1] Detection limit is 0.01 mg·L^{-1}.

Source: NAQUADAT 1985.

6.2.8.4 Forms and Fate in the Aquatic Environment

Boron, with oxidation states of 0 and +3, may form various boranes (hydrides) and organoboron compounds. The environmental chemistry of boron is not well understood (Health and Welfare Canada 1980). Boron is not found in its elemental form in nature, but is usually found in water as a sodium or calcium borate in relatively small quantities (U.S. EPA 1976). The predominant boron species in seawater (76%) is boric acid, H_3BO_3, whereas the borate anion, $B(OH)_4^-$, accounts for approximately 13% (Byrne and Kester 1974). Boric acid is probably the predominant species in fresh water; it is moderately soluble in water and does not readily dissociate (Hem 1970). There is some evidence that boron accumulates in marine zooplankton, algae and seaweeds (Yamamoto *et al.* 1973), although tissue levels are generally low (concentration factors <50) (Bowen 1979).

6.2.8.5 References

Afghan, B.K., P.D. Goulden and J.F. Ryan. 1972. Automated fluorometric method for determination of boron in waters, detergents and sewage effluents. Water Res. 6: 1475.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Byrne, R.H., Jr. and D.R. Kester. 1974. Inorganic speciation of boron in seawater. J. Mar. Res. 32: 119-127.

Chemical Information Services, Ltd. 1980. Directory of World Chemical Producers. 1980/81 edition. Chemical Information Services, Ltd., Oceanside, New York.

CORPUS Information Services. 1978. Boric Acid. CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1980. Borax. CPI Product Profiles. Don Mills, Ontario.

Durfor, C.N. and E. Becker. 1962. Public Water Supplies of the 100 Largest Cities in the U.S. U.S. Government Printing Office, Washington, D.C. U.S. Geol. Surv. Water Supply Pap. 1812. (Cited in Health and Welfare Canada 1980.)

Health and Welfare Canada. 1980. Boron. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 205-213.

Hem, J.D. 1970. Study and Interpretation of the Chemical Characteristics of Natural Waters. U.S. Government Printing Office, Washington, D.C. U.S. Geol. Surv. Water Supply Pap. 1473. pp. 187-188. (Cited in Health and Welfare Canada 1980.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Boron. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 8.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 25-26.

Yamamoto, T., T. Yamaoka, T. Fujita and C. Isoda. 1973. Boron content in marine plankton. Rec. Oceanogr. Works Jpn. 12: 13-21.

6.2.9 Cadmium

6.2.9.1 Uses and Production

Cadmium is used in electroplating other metals or alloys for protection against corrosion, in the manufacture of pigments, nickel-cadmium storage batteries, solders, electronic equipment, lubricants, photography supplies, glass, ceramics and some biocides and as a stabilizer in plastics. Cadmium may also be present in the phosphate rock used for fertilizers. Cadmium compounds are used in the production of polyvinyl chloride (PVC) (cadmium stearate) and tubes for television sets (cadmium phosphors). Cadmium metal is also found in cadmium-silver solders, in telephone and trolley wires (1% cadmium, 99% copper) and in metal sheets for automobile radiator fins (Reeder *et al.* 1979; McNeely *et al.* 1979).

Cadmium is economically recoverable only when found in association with nonferrous metal ores such as zinc, lead and copper (Lymburner 1974; Environment Canada 1976). Since the 1930's, worldwide demand for cadmium has increased steadily to the extent that consumption is now limited essentially by the concentration of cadmium zinc ores and the supply of refined zinc (Lymburner 1974; Hiatt and Huff 1975). Cadmium recovery from zinc ore ranges from 31.5 to 67.5% (70-90% from ore to concentrate and 45-75% from concentrate to metal). Cadmium is recovered from the fumes produced during the roasting of zinc ores and concentrates and from the precipitates obtained during the purification of zinc sulphate (Brown 1977).

Canadian cadmium production was 1602 kg in 1984, up by 24% from production in 1983 (1193 kg). Ontario was the major cadmium producer at 1015 kg (63%) and British Columbia was a distant second at 221 kg (14%) (Energy, Mines and Resources Canada 1985). The following cadmium compounds were imported into Canada in 1982: cadmium oxide (2 t), cadmium sulphide (4 t) and cadmium salts of inorganic acids (1 t) (Statistics Canada 1983).

6.2.9.2 Sources and Pathways for Entering the Aquatic Environment

Cadmium ranks as the 64th element in the earth's crust, with an average crustal abundance of 0.2 $mg \cdot kg^{-1}$ (Taylor 1964). Cadmium commonly occurs as greenockite (CdS), which is found associated with zinc sulphide ore, particularly sphalerite (ZnS) (Brown 1977). Canadian zinc ores contain up to 0.07% recoverable cadmium (Barry 1975). It is estimated that approximately 500 t of cadmium enter the global environment annually as a result of natural weathering phenomena (Bertine and Goldberg 1971).

The main anthropogenic sources of cadmium in the environment are: (1) emissions to air and water from mining, metal (zinc, lead, copper) smelters and industries involved in manufacturing alloys, paints, batteries and plastics; (2) agricultural use of sludges, fertilizers and pesticides containing cadmium; and (3) burning of fossil fuels. The deterioration of galvanized materials also contributes cadmium to the environment (Friberg *et al.* 1974).

The major atmospheric sources of cadmium are iron and steel industries (blast furnace), primary zinc production (especially the roasting phase) and primary copper and nickel production (Bertine and Goldberg 1971; Environment Canada 1976). Because of the low cadmium concentrations in petroleum and coal, 0.01 and 0.002 $mg \cdot kg^{-1}$, respectively, the burning of fossil fuels does not seem to be a major source of cadmium in the environment (Bertine and Goldberg 1971). The most recent Canadian data available on cadmium emissions are from 1972. Total cadmium emissions to the atmosphere in 1972 were estimated at 508 t. The primary copper and nickel industry was the largest contributor, accounting for 78.1% or 397 t of the total. The combustion of fuel in stationary sources accounted for a further 16.9% or 86.5 t. Transportation, solid waste incineration and pesticide application sectors accounted for only <0.7, 0.7 and <0.1% of the total, respectively. Quebec, which is the centre of the Canadian primary copper industry, accounts for 75.1% of total cadmium emissions (Environment Canada 1976).

6.2.9.3 Environmental Concentrations

Cadmium is present in trace concentrations in fresh water, generally less than 1 $\mu g \cdot L^{-1}$, with a range of 0.1-10 $\mu g \cdot L^{-1}$ (Friberg *et al.* 1974; Fleischer *et al.* 1974; Hiatt and Huff 1975; McNeely *et al.* 1979). Concentrations above these background values can be attributed to anthropogenic sources (McNeely *et al.* 1979; Health and Welfare Canada 1980).

Of 3067 samples taken across Canada for total cadmium analysis, only 4 had concentrations above the detection limit of 10 $\mu g \cdot L^{-1}$. Central Canada and the Pacific region had no samples with concentrations above the detection limit. The Western region reported three values (61, 37 and 25 $\mu g \cdot L^{-1}$), and the Atlantic region had only one total cadmium value (12 $\mu g \cdot L^{-1}$) above the detection limit (NAQUADAT 1985).

6.2.9.4 Forms and Fate in the Aquatic Environment

In natural surface waters, cadmium occurs predominantly in the divalent form, comprising several inorganic (e.g. halides, oxides, sulphides) and organic compounds (Reeder *et al.* 1979). The form and fate of cadmium in water are complicated, and depend upon its chemical speciation, which is determined by water pH and hardness as well as the presence of ligands and coexisting metal cations (Florence 1982; Moore and Ramamoorthy 1984). Most of the chemical speciation information pertaining to cadmium is based on theoretical calculations and laboratory studies (U.S. EPA 1979). Carbonates, sulphides and hydroxides of cadmium have very low water solubilities (Reeder *et al.* 1979). In fresh waters, cadmium exists principally as free Cd(II) ion, cadmium chloride and cadmium carbonate (Mantoura *et al.* 1978). Much of the dissolved cadmium in the water column is in the divalent cation form in waters up to about pH 9.0; however, its solubility decreases as water pH increases above pH 9.0 because of the formation of cadmium hydroxide (Moore and Ramamoorthy 1984). Redox potential is believed to have little direct influence on cadmium speciation; however, under reducing conditions and in the presence of sulphur, insoluble cadmium sulphide is produced (Muramoto 1982).

Sorption is probably the most important process for the removal of cadmium from the water column. Exchange of cadmium for calcium ions in the lattice structure of carbonate minerals can remove cadmium from solution. In natural waters, coprecipitation with hydrous iron, aluminum and manganese oxides occurs. Alternatively, in waters of high organic content, adsorption of cadmium to humic substances and other organic complexing agents can be significant (U.S. EPA 1979).

There is no evidence to suggest that photolysis is important in the removal of cadmium from the aquatic environment. There is also no firm evidence that cadmium or cadmium compounds are volatilized (U.S. EPA 1979).

Depending upon its availability for uptake by biota (Florence 1982), cadmium may be accumulated by a number of aquatic organisms, including macrophytes, phytoplankton, zooplankton, invertebrates and fish. Although the degree of bioaccumulation varies with such factors as species and age of organism, bioconcentration factors are in the order of 10^2-10^5 (Reeder *et al.* 1979). In general, uptake of cadmium by aquatic organisms is influenced by water hardness, with tissue concentrations decreasing as water hardness increases (Kinkade and Erdman 1975). Cadmium bioaccumulation generally increases with increasing water temperature (Remacle *et al.*

1982; Rombough and Garside 1982). A reduction in pH leads to greater uptake in bacteria (Pfister 1982) and algae (Hart and Scaife 1977). The presence of complexing agents usually results in a decrease in bioaccumulation (Poldoski 1979). Values of biological half-lives reported in the literature appear to be quite variable, but most studies appear to support a relatively long residence time in fish tissue. For example, biological half-lives in rainbow trout (*Salmo gairdneri*) muscle and carp (*Cyprinus carpio*) muscle were reported to be 248 d (Calamari *et al.* 1982) and 67-136 d (Muramoto 1982), respectively. A biological half-life of more than 1 year was reported for liver and kidneys of rainbow trout (Haux and Larsson 1984). There is no evidence for cadmium biomagnification through the aquatic food web (Wong 1985).

6.2.9.5 References

Barry, G.S. 1975. Cadmium. *In* Canadian Minerals Yearbook 1974. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. (Cited in Reeder *et al.* 1979.)

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Brown, D.H. 1977. Cadmium. *In* Canadian Minerals Yearbook 1976. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. (Cited in Reeder *et al.* 1979.)

Calamari, D., G.F. Gaggino and G. Pacchetti. 1982. Toxicokinetics of low levels of Cd, Cr, Ni and their mixture in long-term treatment on *Salmo gairdneri* Rich. Chemosphere 11: 59-72.

Energy, Mines and Resources Canada. 1985. Canadian mineral production 1983 and 1984. Can. Min. J. 106(2): 26-27.

Environment Canada. 1976. National Inventory of Sources and Emissions of Cadmium (1972). Air Pollution Control Directorate, Environmental Protection Service, Ottawa. Rep. APCD 76-2.

Fleischer, M., A.F. Sarofim, D.W. Fassett, P. Hammond, H.T. Shacklette, I.C.T. Nisbet and S. Epstein. 1974. Environmental impact of cadmium: a review by the panel on hazardous trace substances. Environ. Health Perspect. Exp. Iss. 7: 253-323. (Cited in Health and Welfare Canada 1980.)

Florence, T.M. 1982. The speciation of trace elements in water. Talanta 29: 345-364.

Friberg, L., M. Piscator, G.F. Nordberg and T. Kjellström. 1974. Cadmium in the Environment. Chemical Rubber Co. Press Inc., Cleveland, Ohio. (Cited in Reeder *et al.* 1979.)

Hart, B.A. and P.D. Scaife. 1977. Toxicity and bioaccumulation of cadmium in *Chlorella pyrenoidosa*. Environ. Res. 14: 401-413.

Haux, C. and A. Larsson. 1984. Long-term sublethal physiological effects on rainbow trout, *Salmo gairdneri*, during exposure to cadmium and after subsequent recovery. Aquat. Toxicol. 5: 129-142.

Health and Welfare Canada. 1980. Cadmium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 215-236.

Hiatt, V. and J.E. Huff. 1975. The environmental impact of cadmium: an overview. Int. J. Environ. Stud. 7: 277-285. (Cited in Health and Welfare Canada 1980.)

Kinkade, M.L. and H.E. Erdman. 1975. The influence of hardness components (Ca^{2+} and Mg^{2+}) in water on the uptake and concentration of cadmium in a simulated freshwater ecosystem. Environ. Res. 10: 308-317.

Lymburner, D.B. 1974. Environmental Contaminants Inventory Study No. 2. The Production, Use and Distribution of Cadmium in Canada. Inland Waters Directorate, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario. Rep. Ser. No. 39.

Mantoura, R.F.C., A. Dickson and J.F. Riley. 1978. The complexation of metals with humic materials in natural waters. Estuarine Coastal Mar. Sci. 6: 387-408.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Cadmium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 8-9.

Moore, J.W. and S. Ramamoorthy. 1984. Heavy Metals in Natural Waters. Applied Monitoring and Impact Assessment. Springer-Verlag, New York. 268 pp.

Muramoto, S. 1982. Reductions of Cd in a Cd-contaminated fish by long-term exposure to EDTA or freshwater. J. Environ. Sci. Health A17: 67-74.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Pfister, R.M. 1982. Evaluation of Bacterial Binding and Release of Cadmium from Aquatic Sediments. U.S. Dep. of the Interior Rep. 712437. 115 pp.

Poldoski, J.E. 1979. Cadmium bioaccumulation assays. Their relationship to various ionic equilibria in Lake Superior water. Environ. Sci. Technol. 13: 701-706.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979. Cadmium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Remacle, J., C. Houba and J. Ninane. 1982. Cadmium fate in bacterial microcosms. Water Air Soil Pollut. 18: 455-465.

Rombough, P.J. and E.T. Garside. 1982. Cadmium toxicity and accumulation in eggs and alevins of Atlantic salmon, *Salmo salar*. Can. J. Zool. 60: 2006-2014.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285.

U.S. EPA. 1979. Cadmium. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 9-1 to 9-20.

Wong, P.T.S. 1985. Personal communication. Great Lakes Fisheries Research Branch, Canada Centre for Inland Waters, Burlington, Ontario.

6.2.10 Calcium

6.2.10.1 Uses and Production

Calcium oxide is used extensively in mortar, stucco and plaster in the building industry, and in pulp and paper production, sugar refining, petroleum refining and tanning (McQuarrie 1966). Calcareous materials are used in chemical industries in the form of limestone, lime, calcium cyanamide, and calcium arsenates, carbides and chlorides. Lime is widely used in water and wastewater treatment. Calcium is used in the brewing industry, in glue manufacturing and in road salting (McNeely *et al.* 1979; Health and Welfare Canada 1980). Because Chromasco Ltd., at Haley (near Renfrew), Ontario, is the only calcium producer in Canada, data on Canadian production, consumption and exportation are not published for reasons of confidentiality (McCutcheon 1984). Western world calcium production in 1982 in Canada, France, Japan and the U.S.A. was estimated to be about 1360 t. Canadian production was estimated to be about 35% of western world production (U.S. Department of the Interior 1982). Importation data are available for calcium and many calcium compounds, and are presented in Table 6-8.

6.2.10.2 Sources and Pathways for Entering the Aquatic Environment

Calcium is one of the most abundant cations in surface waters and groundwaters. It is readily soluble in water and enters the aquatic environment through the weathering of

Table 6-8. Importation of Calcium and Calcium Compounds into Canada

Compound	Amount (t) 1981	Amount (t) 1982
Calcium (metal)	24	50
Calcium cyanide (formulated fumigant)	1	—
Calcium sulphate dihydrate	23	54
Calcium chloride (dry weight)	7144	9096
Calcium oxide	4	2
Calcium phosphates (not specified/inorganic)	4262	3022
Calcium hydroxide	62	47
Calcium arsenate (formulated pesticide)	—	2
Calcium peroxide	2	5
Calcium carbide	8108	1716
Calcium chloride (liquid/dry weight)	4126	3750
Calcium cyanamide (less than 25% nitrogen content)	122	91
Calcium nitrate (less than 16% nitrogen content)	4475	5181

Source: Statistics Canada 1983.

rocks, especially limestone, and from the soil, through seepage and runoff. Calcium salts, along with those of magnesium, are primarily responsible for the hardness of water (McNeely *et al.* 1979). The leaching of calcium from soil has been found to increase significantly with the acidity of rainwater (Harvey *et al.* 1979). Silicate minerals, such as pyroxenes and amphiboles, sedimentary deposits of calcite and dolomite, gypsum and the mineral apatite [$Ca_5(PO_4)_3(F,Cl,OH)$], may release substantial amounts of calcium into waters (McNeely *et al.* 1979).

Industrial effluent loadings of calcium to Lake Superior and Lake Huron during the period between 1973 and 1975 were 14.8×10^3 and 6.2×10^3 t·a^{-1}, respectively (IJC 1976). A sample taken in 1980 from a British Columbia industrial wastewater station of NAQUADAT had a dissolved calcium concentration of 65.5 mg·L^{-1} (detection limit 0.5 mg·L^{-1}) (NAQUADAT 1985).

It is estimated that 14×10^5 t of calcium were released into the atmosphere during 1967 as a result of the combustion of fossil fuels in the northern hemisphere (Bertine and Goldberg 1971). The atmospheric loading of calcium in the Great Lakes Basin is estimated to be more than 1×10^5 t (IJC 1976, 1977).

6.2.10.3 Environmental Concentrations

The concentrations of calcium in natural fresh waters vary according to the proximity of calcium-rich geological formations. Typical calcium concentrations are less than 15 mg·L^{-1}, whereas waters close to carbonate rocks may have concentrations in the range of 30-100 mg·L^{-1}. Waters in contact with gypsiterous shale may have a calcium concentration of several hundred milligrams per litre. Seawater concentrations of calcium are usually 400 mg·L^{-1}, and brines may contain up to 75 000 mg·L^{-1} (McNeely *et al.* 1979).

Environmental concentration ranges for calcium in Canadian surface waters are presented in Table 6-9. Calcium concentrations gradually increase from Lake Superior (13 mg·L^{-1}) to Lake Ontario (36 mg·L^{-1}), reflective of the geochemistry of the regions and the extent of anthropogenic influences (IJC 1977).

Table 6-9. Environmental Concentration Ranges for Calcium in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	1.19^{1}-62.3	1 584	1980-1985
Western	274^{2}-474	3	Prior to 1980
	ND^{1,3}-137.0	30 489	1980-1985
Central	ND^{2}-349.0	2 772	Prior to 1980
	0.28^{1}-67.0	4 378	1980-1985
Atlantic	0.4^{2}-11.0	66	1980
	0.22^{1}-260.0	1 432	1980-1985

[1] Detection limit is 0.5 mg·L^{-1} (dissolved).
[2] Detection limit is 0.002 mg·L^{-1} (total).
[3] ND = not detected.

Source: NAQUADAT 1985.

6.2.10.4 Forms and Fate in the Aquatic Environment

Calcium is strongly electropositive and is characterized by a valence of +2 in compounds (Goodenough and Stenger 1973; Cotton and Wilkinson 1980). Calcium compounds are stable in water in the presence of carbon dioxide. The calcium content of aquatic systems decreases markedly because of the precipitation of calcium salts (e.g. $CaCO_3$), which occurs as a result of increases in water temperature, a reduction in pressure causing degassing of carbon dioxide and photosynthetic activity (Hutchinson 1957; Loewenthal and Marais 1976).

The calcium content of soft-water lakes (well below saturation levels) shows minor seasonal variations with depth compared with the marked seasonal dynamics prevalent in hard-water lakes. Calcium levels in hard-water systems decrease markedly as a result of precipitation of $CaCO_3$ during the summer months. The $CaCO_3$ coprecipitates with inorganic nutrients, and also removes humic acids and other organic compounds by adsorption. Some of the $CaCO_3$ is entrained permanently in the sediments. Calcium complexes with humic acids, especially in the sediments, hence altering exchange equilibria in the hypolimnion of water bodies (Ohle 1955). Calcium commonly constitutes >30% of the sediments by weight in moderately hard-water lakes (Wetzel 1970). The biogenically induced decalcification of a lake's epilimnion reaches an extreme in very productive hard waters (Wetzel 1975).

Calcium is considered to be an essential element for all organisms, with the possible exception of some fungi, and is accumulated in some red algae, the shells of many invertebrates and mammalian bone. The calcium contents of aquatic biota (marine algae, 4000-24 000 mg·kg^{-1}; marine fish, 76-20 000 mg·kg^{-1}) and mammals (muscle, 140-700 mg·kg^{-1}; bone, 170 000 mg·kg^{-1}) have been reported (Bowen 1979).

6.2.10.5 References

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Cotton, P.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Goodenough, R.D. and V.A. Stenger. 1973. Magnesium, calcium, strontium, barium and radium. *In* Comprehensive Inorganic Chemistry. Vol. I. J.C. Bailar, Jr., H.J. Emeleus, Sir R. Nyholm and A.F. Trotman-Dickenson (eds.). Pergamon Press, Oxford. pp. 591-664.

Harvey, H.H., R.C. Pierce, P.J. Dillon, J.R. Kramer and D.M. Whelpdale. 1981. Acidification in the Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18475. 369 pp.

Health and Welfare Canada. 1980. Calcium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 237-246.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics, and Chemistry. John Wiley & Sons, New York. 1015 pp.

IJC. 1976. The Waters of Lake Huron and Lake Superior. Vol. I. Summary and Recommendations. Report by the Upper Lakes Reference Group, International Joint Commission, Windsor, Ontario.

IJC. 1977. Atmospheric Loadings of the Lower Great Lakes and the Great Lakes Drainage Basin. Report by the International Reference Group, International Joint Commission, Windsor, Ontario.

Loewenthal, R.E. and G.V.R. Marais. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Application. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 433 pp.

McCutcheon, W. 1984. Calcium. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 10.1-10.2.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Calcium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 9-10.

McQuarrie, M.C. 1966. Lime. *In* McGraw-Hill Encyclopedia of Science and Technology. McGraw-Hill, Toronto, Ontario.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ohle, W. 1955. Ionenaustausch der Gewässersedimente. Mem. Ist. Ital. Idrobiol. 8 (Suppl.): 221-245. (Cited in Wetzel 1975.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. Department of the Interior. 1982. Calcium. *In* Mineral Facts and Problems. 1980 edition. Bureau of Mines, Washington, D.C. (Cited in McCutcheon 1984.)

Wetzel, R.G. 1970. Recent and postglacial production rates of a marl lake. Limnol. Oceanogr. 15: 491-503.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.11 Calcium Carbonate Saturation

The formation of scale or sludge in water distribution systems may induce equipment failures. Common scale deposits can consist of calcium carbonate, phosphate, silicate or sulphate, or of magnesium hydroxide, phosphate or silicate. Scale may also be formed from oxides, silica or related substances. Conversely, deterioration of metals caused by corrosion may produce dissolved metal ions that may redeposit as oxides. Increases in the corrosive tendency of water can arise as a result of the presence of water constituents, such as dissolved oxygen, carbon dioxide and anions such as chloride and sulphate, and low pH. Microorganisms, such as sulphate-reducing or iron bacteria, can also be involved in corrosion and/or deposit formation. It is generally assumed that a thin protective layer of calcium carbonate on metal surfaces is often effective in preventing corrosion in water distribution systems (Greenberg *et al.* 1981).

The pH at which water is just saturated with calcium carbonate ($CaCO_3$) is known as the pH of saturation (pH_s). It may be related to the actual pH of the water by the Langelier Saturation Index (SI), defined as:

$$SI = pH - pH_s$$

This index is not directly related to corrosion; however, deposition of a thin layer of $CaCO_3$ scale is considered to be protective. Hence, a slight positive index is frequently associated with noncorrosive conditions, whereas a negative index indicates the potential for corrosion. Stable water usually has a zero or slightly positive index. Another index, called the Ryzner Stability Index (RSI), is defined as:

$$RSI = 2pH_s - pH$$

and has a positive value. Since both indexes are based on carbonate equilibria in water (see Section 6.2.20), they will be affected by temperature, ionic strength and alkalinity of the water in the distribution system (Greenberg *et al.* 1981).

6.2.11.1 References

Greenberg, A.E., J.J. Connors and D. Jenkins. 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

6.2.12 Chloride

6.2.12.1 Uses and Production

Chloride, in the form of sodium chloride and calcium chloride, is used extensively for snow and ice removal. Calcium chloride is also used for tire ballasting, oil well cementing, freeze-proofing of ores, coal or aggregates and wastewater treatment. In 1979, 79% of $CaCl_2$ was sold for road building, base stabilization and dust control (Environment Canada 1984). The chemical industry is the second largest consumer of sodium chloride (one-third of domestic production). Industrial uses include the manufacture of sodium hydroxide, chlorine, sodium carbonate, sodium chlorate, sodium bicarbonate, sodium chlorite and sodium hypochlorite (NRCC 1977). Ninety-five percent of potassium chloride (potash) is used for the production of fertilizers; the remainder is used to manufacture products such as matches, vat dyes, glassware, china, pharmaceuticals, detergents, fumigants and insecticides (NRCC 1977).

Canadian production and importation of these chloride compounds are presented in Table 6-10.

6.2.12.2 Sources and Pathways for Entering the Aquatic Environment

Chloride is widely distributed in the environment, generally as sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride ($CaCl_2$) (NRCC 1977). Chlorides may be found in sulphatic and calcareous deposits. The weathering and leaching of sedimentary rocks and soils and the dissolution of

Table 6-10. Production and Importation of Three Major Chloride Compounds in Canada

Compound (year)	Production (t)	Importation (t)
Calcium chloride (1979)	114 000	11 840
Sodium chloride (1982)	7 972 644	1 526 879
Potassium chloride (1983)	6 293 747	2 277

Sources: CORPUS Information Services 1981; Barry 1985; Prud'homme 1985.

salt deposits release chlorides to water (McNeely *et al.* 1979). Other sources of chlorides to surface water and groundwater include the salting of highways, effluents from chemical industries, oil well operations, sewage, irrigation drainage and refuse leachates and salt water intrusion (Health and Welfare Canada 1980). An estimated 25-50% of applied road salt can enter groundwater (McConnell and Lewis 1972). In maritime coastal regions, local surface and groundwater contamination may result from the atmospheric transport of chlorides in sea spray (McNeely *et al.* 1979). Generally, atmospheric concentrations are low, with the exception of coastal areas (as a result of sea spray) and areas near sodium chloride and potassium chloride mining and processing industries (Health and Welfare Canada 1980).

6.2.12.3 Environmental Concentrations

Approximately 0.05% of the lithosphere consists of chloride, with the greatest amount found in the oceans (Health and Welfare Canada 1980). In natural surface waters, chlorides are present in low concentrations, usually less than 10 mg·L^{-1} and often less than 1 mg·L^{-1} (Bond and Straub 1973; NAQUADAT 1976). Concentrations of chloride vary according to climatic region; surface waters in humid regions contain low chloride concentrations (<10 mg·L^{-1}), whereas waters in semi-arid and arid regions contain as much as several hundred milligrams per litre (McNeely *et al.* 1979). The Great Lakes and St. Lawrence Lowland waters contain higher concentrations (20 mg·L^{-1}) because of industrial activity (NRCC 1977). Lake Erie concentrations increased threefold in 50 years, 70% of which resulted from road salting, municipal wastewaters and industrial sources (Wetzel 1975). Concentrations as high as 600 and 770 mg·L^{-1} recorded in Lake Manitoba and Lake Winnipegosis during 1973 to 1977 have been attributed to natural sources (Morelli 1986). Municipal wastewater from a station sampled in Newfoundland reported maximum concentrations of 1020 and 1180 mg·L^{-1} of dissolved chloride in 1982 and 1983, respectively (NAQUADAT 1985). "Standard" seawater may have as much as 19 300 mg·L^{-1}, and brines may contain up to 200 000 mg·L^{-1} (McNeely *et al.* 1979). In general, low chloride concentrations have been recorded for several Canadian provinces (<10 mg·L^{-1}) (NAQUADAT 1976).

Environmental concentration ranges for chloride in Canadian surface waters are presented in Table 6-11.

6.2.12.4 Forms and Fate in the Aquatic Environment

Chloride ion is a major constituent of most waters. Although chloride is the dominant anion in marine and closed drainage systems (e.g. playa lakes), it is rarely dominant in open drainage systems. Three-quarters of the chlorine on the earth's surface occurs as chloride (Cl$^-$) in solution. The disinfection of raw waters or sewage will contribute chloride ions to receiving waters (see Section 6.2.13) (NRCC 1977).

Table 6-11. Environmental Concentration Ranges for Dissolved Chloride in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	<0.1-27.0	1556	1980-1981
Western	0.1-473.0	2412	Prior to 1980
Central	<0.1-450.0	5221	1980-1983
Atlantic	0.04[2]-861.0	9552	1980-1984

[1] Detection limit is 0.1 mg·L^{-1}.

[2] Detection limit is 0.01 mg·L^{-1}.

Source: NAQUADAT 1985.

6.2.12.5 References

Barry, G.S. 1985. Potash. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

Bond, R.G. and C.P. Straub. 1973. Handbook of Environmental Control. Vol. 3. Chemical Rubber Co., Cleveland, Ohio.

CORPUS Information Services. 1981. Calcium Chloride. CPI Product Profiles. Don Mills, Ontario.

Environment Canada. 1984. Calcium Chloride. Environmental and Technical Information for Problem Spills (EnviroTIPS). Environmental Protection Service, Ottawa. 76 pp.

Health and Welfare Canada. 1980. Chloride. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 247-254.

McConnell, H.H. and J. Lewis. 1972. Add salt to taste. Environment 14(9): 38-44.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Halides – chloride. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 16-17.

Morelli, M. 1986. Personal communication. Environmental Standards and Studies, Manitoba Environment and Workplace Safety and Health, Winnipeg, Manitoba.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1977. Effects of Alkali Halides in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15019. 171 pp.

Prud'homme, M. 1985. Salt. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.13 Chlorine

6.2.13.1 Uses and Production

Chlorine is used primarily in the chemical industry for the production of organic and inorganic products. Another major user of chlorine is the pulp and paper industry. Chlorine is used in water to destroy or deactivate disease-producing organisms in both the purification process of domestic water supplies and the treatment of effluent from sewage treatment plants (Pierce 1978; Ontario Ministry of the Environment 1981), textile mills, power plants and other industries. Its disinfectant, oxidative capacity and adaptability as a coagulant make chlorine useful in wastewater treatment. Chlorine also controls fouling by biological material of heat-exchange surfaces in freshwater and marine cooling circuits (Pierce 1978).

In 1982, 1 233 300 t of chlorine were produced in Canada, and 21 400 t were imported (CORPUS Information Services 1983).

6.2.13.2 Sources and Pathways for Entering the Aquatic Environment

One source of chlorine in water is the purification and treatment of water supplies and wastewaters. Of the total amount of chlorine used in Canada each year, approximately 4% is utilized for potable water treatment, 3% for wastewater treatment and 2% for water facilities operated by industry. The remaining 91% is distributed among pulp and paper, textile and other chemical industries (Pierce 1978). Some chlorine may enter the aquatic environment through atmospheric sources, and small amounts may be produced by the action of sunlight on chloride-containing aerosols (NAS 1976).

6.2.13.3 Environmental Concentrations

Chlorine usually does not persist for extended periods in water (Ontario Ministry of the Environment 1979). Many wastewater treatment plants are required to maintain a residual chlorine concentration of 0.5-2.0 $mg \cdot L^{-1}$ during treatment (Ontario Ministry of the Environment 1979). Chlorine is rapidly converted to chloride in receiving waters (Thomas 1964). Sampling results for chlorine are not reported in NAQUADAT.

6.2.13.4 Forms and Fate in the Aquatic Environment

Gaseous chlorine, when dissolved in water in the absence of nitrogenous or other interfering substances, is rapidly hydrolyzed to hypochlorous acid (HOCl) and hydrochloric acid (HCl). Hydrochloric acid readily dissociates to hydrogen and chloride ions. Hypochlorous acid partially dissociates to hydrogen ions and hypochlorite ions (^{-}OCl) ($K_d = 1.45 \times 10^{-4}$ at 0°C) (Liebhafsky 1934). The relative proportions of Cl_2, HOCl and ^{-}OCl in equilibrium (collectively referred to as free available chlorine) are governed by pH, temperature and ionic strength. Below pH 2, Cl_2 is the dominant species. Between pH 2 and 7, the equilibrium overwhelmingly favours HOCl. At pH 7.4 and 20°C, in water of low ionic strength, the equilibrium mixture is composed of equimolar concentrations of HOCl and ^{-}OCl. At temperatures lower than 20°C, the equilibrium is shifted in favour of HOCl and ^{-}OCl at pH values between 2 and 7 (Pierce 1978). When chlorine is added to seawater in the absence of nitrogenous substances, hypobromous acid is rapidly formed, with the result that the majority of the chlorine is reduced to chloride ion (Pierce 1978).

Chlorine in water readily reacts with nitrogenous substances to yield mono-, di- and triamines, *N*-chloramines and *N*-chloramides and other *N*-chlorinated compounds (collectively referred to as combined available chlorine). Monochloramine (NH_2Cl) is considered to be the principal component of the combined available chlorine in aqueous solution. It has been found to be relatively stable in aqueous media, with detectable levels being found after several days in water treatment distribution systems (Kinman and Layton 1976).

Both free and combined forms of chlorine may readily participate in a variety of reactions with organic compounds to yield chlorinated products (Pierce 1978). The chlorine remaining in water after treatment is termed residual chlorine. The total of free and combined chlorine is referred to as total residual chlorine (TRC). The measurement of TRC is considered to be sufficient to define toxicity to freshwater aquatic organisms (Brungs 1973; Pierce 1978). It has been assumed that TRC would not persist in aquatic systems because the chlorine demand of receiving waters results in the rapid formation of chloride ions. TRC has been found, however, to persist up to several days in chlorinated sewage effluents (Esvelt *et al.* 1973; Servizi and Martens 1974).

6.2.13.5 References

Brungs, W.A. 1973. Effects of residual chlorine on aquatic life. J. Water Pollut. Control Fed. 45: 2180-2193.

CORPUS Information Services. 1983. Chlorine. CPI Product Profiles. Don Mills, Ontario.

Esvelt, L.A., W.J. Kaufman and R.E. Selleck. 1973. Toxicity assessment of treated municipal wastewaters. J. Water Pollut. Control Fed. 45: 1558-1572.

Kinman, R.N. and R.F. Layton. 1976. New method for water disinfection. J. Am. Water Works Assoc. 68: 298-302.

Liebhafsky, H.A. 1934. The equilibrium constant of the bromine hydrolysis and its variation with temperature. J. Am. Chem. Soc. 56: 1500-1505.

NAS. 1976. Chlorine and Hydrogen Chloride. Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Ontario Ministry of the Environment. 1979. Rationale for the Establishment of Ontario's Provincial Water Quality Objectives. Water Resources Branch, Toronto, Ontario. 236 pp.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Pierce, R.C. 1978. The Aqueous Chlorination of Organic Compounds – Chemical Reactivity and Effects in Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16450. 136 pp.

Servizi, J.A. and D.W. Martens. 1974. Preliminary Survey of Toxicity of Chlorinated Sewage to Sockeye and Pink Salmon. Int. Pacific Salmon Fish. Comm., Prog. Rep. No. 30. New Westminster, British Columbia. 42 pp.

Thomas, J.F.J. 1964. Surface water quality in major drainage basins and northern areas of Canada. J. Am. Water Works Assoc. 56: 1173-1193.

6.2.14 Chromium

6.2.14.1 Uses and Production

Hexavalent chromium compounds are used in the metallurgical industry for chrome alloy and chromium metal production, in the chemical industry as oxidizing agents in chrome plating, and in the production of other chromium compounds used in paints, dyes, explosives, ceramics and paper. Trivalent chromium salts are used in textile dyeing, in the ceramic and glass industry and in photography. Chromium compounds are added to drilling muds to reduce the corrosion fatigue of drilling pipes. Other applications include its use in heating and cooling coils and fire sprinkler systems. It is also present in some fertilizers and pesticides (McNeely *et al.* 1979; Taylor *et al.* 1979; Health and Welfare Canada 1980).

Canadian deposits of chromium (chromite) are usually of low grade or uneconomical to mine (Law-West 1984). Canadian requirements for chromite are filled by importation, which was 47 626 t in 1981. Canadian consumption of chromite in 1981 was 24 771 t. Canada imports all its chromium largely in the form of chromite ore and ferrochromium. In 1981, 31 573 t of ferrochromium were imported, and its consumption amounted to 29 547 t (Law-West 1984).

6.2.14.2 Sources and Pathways for Entering the Aquatic Environment

Chromite ($FeCr_2O_2$) is the predominant chromium-bearing mineral. Chromium in rocks and soil is generally present as insoluble chromium oxide (Taylor *et al.* 1979).

Weathering is the main natural process by which chromium is released into the environment (McNeely *et al.* 1979); approximately 200 000 $t \cdot a^{-1}$ of chromium enter the environment globally by this process (Bertine and Goldberg 1971). There are also several anthropogenic activities which cause chromium to enter the environment; the estimated amount of chromium released worldwide as a result of these activities is 77 700 $t \cdot a^{-1}$. The major sources of chromium emissions are ferrochromium production (57.9%) and metal plating (25.7%). Other processes, such as coal and oil burning, refractory production, cement manufacturing and the production of chromium steels, account for the remaining 16.4% (Taylor *et al.* 1979).

In Canada, estimated chromium emissions from cement manufacturing in 1975 ranged from 3 to 63 t (Taylor *et al.* 1979). In the same year, chromium released to the environment through the metal plating industry was estimated at 230 t (Environment Canada 1976).

6.2.14.3 Environmental Concentrations

Chromium is generally present at low concentrations in Canadian surface waters (Health and Welfare Canada 1980). Water samples from the Great Lakes had chromium concentrations between 0.2 and 19 $\mu g \cdot L^{-1}$, with an average value of 1.0 $\mu g \cdot L^{-1}$ (Durum and Haffty 1961; Weiler and Chawla 1969). Chromium concentrations in Canadian rivers were between 1.0 and 23 $\mu g \cdot L^{-1}$ (range 0.2-19 $\mu g \cdot L^{-1}$) (Durum and Haffty 1961). Chromium concentrations along the length of the Ottawa River varied from 0.24 to 1.31 $\mu g \cdot L^{-1}$ (Merritt 1975).

NAQUADAT (1985) data on total chromium sampled during the period 1980-1985 showed values ranging from 2 $\mu g \cdot L^{-1}$ (the detection limit) to 44 $\mu g \cdot L^{-1}$ for the Central region. The Atlantic region reported a range of 2 $\mu g \cdot L^{-1}$ (the detection limit) to 24 $\mu g \cdot L^{-1}$ for total chromium. No total chromium sampling was done in the Western and Pacific regions during this time period (NAQUADAT 1985).

Few data are available on levels of chromium in drinking water (Health and Welfare Canada 1980). In the U.S.A., chromium concentrations above 1.0 $\mu g \cdot L^{-1}$ in drinking water were detected in only 11% of the 969 water systems tested; the average concentration of chromium in these samples was 2.3 $\mu g \cdot L^{-1}$ (Craun and McCabe 1975).

6.2.14.4 Forms and Fate in the Aquatic Environment

Chromium can exist in oxidation states ranging from −2 to +6, but is present in aqueous systems mainly in the trivalent (Cr(III); chromic compounds) and hexavalent (Cr(VI); chromates and dichromates) states (U.S. EPA 1979; Health and Welfare Canada 1980).

The trivalent form of chromium is a positively charged ion that has a strong tendency to form stable complexes with negatively charged inorganic or organic species (McNeely *et al.* 1979). If there are no anionic species present, Cr(III) in neutral solutions forms colloidal hydrous oxides. Thus, it is very unlikely that much dissolved chromium will be present in aqueous solution. Chromium(III) is least soluble in the pH range of natural waters (NRCC 1976; Taylor *et al.* 1979). Precipitation of chromium hydroxide is thought to be the dominant removal mechanism for chromium in natural waters (U.S. EPA 1979). One study showed that the ratio of Cr(III)/Cr(VI) in lake water was affected by the amount of organic matter and dissolved oxygen; the higher the amount of organic matter, the greater the proportion of Cr(III) (Benes and Steinnes 1975).

The hexavalent form of chromium is quite soluble, existing in solution as a complex anion, and is not sorbed to any significant degree by soil or particulate matter. Hence, it is more mobile than Cr(III), and not as susceptible to sedimentation. Cr(VI) reacts strongly with oxidizable substances, usually organic molecules, with the resultant formation of Cr(III). In water containing very little organic material, Cr(VI) is stable for long periods of time. Under aerobic conditions, Cr(VI) is stable in natural waters. Under anaerobic conditions, Cr(VI) is reduced to Cr(III), which hydrolyzes and deposits as chromium oxide at neutral or slightly alkaline pH (Cheremisinoff and Habib 1972; Taylor *et al.* 1979).

In the presence of hydrogen sulphide, Cr(VI) will be reduced to trivalent chromium, which will probably be removed from the water column by sorption (U.S. EPA 1979).

There is no evidence to suggest that photolysis or volatilization of chromium compounds plays an important role in determining the fate of chromium in the aquatic environment. Although there is some speculation that chromium may be methylated in reducing environments, no evidence was found that this process occurs in natural waters (U.S. EPA 1979).

Chromium is bioaccumulated by aquatic organisms (bioconcentration factors (BCF) ≃ 10^2-10^3). Residue levels in aquatic biota are, however, usually lower than levels in sediments (U.S. EPA 1979). Chromium(VI) is able to penetrate cell membranes to a much greater extent than Cr(III), which is one reason why Cr(VI) is considered to be the more toxic form of the metal (U.S. EPA 1973). Biological half-lives of 1-7 d were found for whole-body elimination of Cr(VI) from rainbow trout (*Salmo gairdneri*) (Van der Putte 1981). Chromium does not appear to biomagnify through the aquatic food web (EIFAC 1983).

6.2.14.5 References

Benes, P. and E. Steinnes. 1975. Migration forms of trace elements in natural fresh waters and the effect of water storage. Water Res. 9: 741-749.

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Cheremisinoff, P.N. and Y.H. Habib. 1972. Cadmium, chromium, lead, mercury: a plenary account for water pollution. Water Sewage Works 119: 73-86.

Craun, G.F. and L.J. McCabe. 1975. Problems associated with metals in drinking water. J. Am. Water Works Assoc. 67: 593-599.

Durum, W.H. and J. Haffty. 1961. Occurrence of Minor Elements in Water. U.S. Geol. Surv. Circ. 445. (Cited in Health and Welfare Canada 1980.)

EIFAC (European Inland Fisheries Advisory Commission). 1983. Water Quality Criteria for European Freshwater Fish. Report on Chromium and Freshwater Fish. Food and Agricultural Organization of the United Nations, Rome. EIFAC Tech. Pap. No. 43. 31 pp.

Environment Canada. 1976. Wastewater and Sludge Control in the Canadian Metal Finishing Industry. Water Pollution Control Directorate, Environmental Protection Service, Ottawa. Rep. No. EPS 3-WP-76-10.

Health and Welfare Canada. 1980. Chromium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 255-268.

Law-West, D.G. 1984. Chromium. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report No. 32.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Chromium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 12-13.

Merritt, W.F. 1975. Variation in trace element concentrations along the length of the Ottawa River. Can. J. Earth Sci. 12: 850-857.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1976. Effects of Chromium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15017. 168 pp.

Taylor, M.C., S.W. Reeder and A. Demayo. 1979. Chromium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

U.S. EPA. 1979. Chromium. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Organics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 10-1 to 10-10.

Van der Putte, I., J. Lubbers and Z. Kolar. 1981. Effect of pH on uptake, tissue distribution and retention of hexavalent chromium in rainbow trout (*Salmo gairdneri*). Aquat. Toxicol. 1: 3-18.

Weiler, R.R. and V.K. Chawla. 1969. Dissolved mineral quality of Great Lakes waters. *In* Proc. 12th Conf. on Great Lakes Research, May 5-7, Ann Arbor, Michigan. pp. 801-818.

6.2.15 Cobalt

6.2.15.1 Uses and Production

Cobalt is used in superalloys where it improves the strength, wear and corrosion resistance characteristics of the alloys at elevated temperatures, e.g. in turbine blades for aircraft jet engines and gas turbines for gas pipelines. Cobalt-based superalloys contain 45% or more cobalt, whereas nickel- and iron-based superalloys contain 8-20% cobalt. Cobalt is used where high abrasive resistance is needed, in the coating of tools and in the production of magnets (Telewiak 1985).

Cobalt powder is used as a binder in making cemented tungsten carbides for heavy-duty and high-speed cutting tools. Cobalt oxide is an important additive in paint, glass and ceramics. Cobalt is also of importance in tire and appliance manufacture and in the petroleum industry (Telewiak 1985).

Cobalt is produced as a by-product of nickel-copper production. Ontario and Manitoba are the largest producers in Canada; a total of 2325 t was produced in 1984, up from 1584 t in 1983 (Telewiak 1985).

Western world consumption of cobalt in 1983 and 1984 was 14 800 and 17 500 t, respectively, the largest consumer being the U.S.A. The 1983 consumption in Canada of cobalt metal, oxides and salts was 101 t. In the first 9 months of 1984, Canada exported 1112 t of cobalt metal and 302 t of cobalt oxides and hydroxides. Thirty tonnes (of all forms) were imported (Telewiak 1985).

6.2.15.2 Sources and Pathways for Entering the Aquatic Environment

Cobalt is present in a number of rock types, including granite, basalt, shale, limestone and sandstone. Its crustal abundance averages about 25 mg·kg^{-1}. Common cobalt minerals contain sulphur, arsenic and copper: e.g. linnaeite Co_3S_4, carrollite $CuCo_2S_4$, safflorite $CoAs_2$, skutterudite $(Co,Fe)As_3$ and cobaltite (Co,Fe)AsS. One of the better-known cobalt deposits is the nickel-copper sulphide ores of the Sudbury district in Ontario. Cobalt is also associated with arsenic and antimony in polymetallic sulphide ores and in lead, zinc and copper sulphide ores. Streams and sediments from regions containing cobalt-rich ores contain elevated levels of cobalt compared with levels in water in other areas (Smith and Carson 1981).

Anthropogenic sources of cobalt in the environment include acid coal mine drainage and emissions from coal burning and other industries; dump disposal of products containing cobalt; the addition of cobaltous sulphate to phosphate fertilizers for application to cobalt-deficient soils or direct spraying; road sides and street dusts which contain small amounts of cobalt; and soils near smelters which can have elevated cobalt contents. Up to 60 kg·d^{-1} are discharged by 10 southern Ontario sewage treatment plants to Lake Ontario. Raw sewage contains 2-40 μg·L^{-1} cobalt; primary and secondary effluents contain 1-30 μg·L^{-1} (Smith and Carson 1981).

6.2.15.3 Environmental Concentrations

The amount of cobalt in aerobic surface waters is generally very small. Except where there is gross heavy metal contamination, the concentration of cobalt in freshwater sediments is generally below 20 mg·L^{-1} (Smith and Carson 1981). In general, cobalt concentrations increase during fall circulation and winter, primarily in organic fractions (Benoit 1957; Parker and Hasler 1969).

Environmental concentration ranges for cobalt in Canadian surface waters are presented in Table 6-12.

Table 6-12. Environmental Concentration Ranges for Cobalt in Canadian Surface Waters

Region	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<1[1]	47	Prior to 1980
Western	<1[2]-47	1754	1980-1985
Atlantic	<1[1]	95	1980-1985

[1] Detection limit is 1 $\mu g \cdot L^{-1}$ (total).

[2] Detection limit is 2 $\mu g \cdot L^{-1}$ (total recoverable).

Source: NAQUADAT 1985.

6.2.15.4 Forms and Fate in the Aquatic Environment

Cobalt exists in six oxidation states: −1, 0, +1, +2, +3 and +4; however, only the cobaltous (Co(II)), and cobaltic (Co(III)) forms are common in aqueous solution (Cotton and Wilkinson 1980). Univalent cobalt is of biochemical significance in relation to vitamin B_{12}, of which it constitutes 4.35% by weight (Young 1979). Uncomplexed cobaltous ion is stable in aqueous solution, but the cobaltic ion is a powerful oxidizing agent unless it is present in an anhydrous crystal lattice or is complexed with such ligands as ammonia, ethylenediamine, cyanide or dimethylglyoxime (Trisdan *et al.* 1981).

The predominant cobalt species in natural fresh waters are Co(II), carbonate, hydroxide, sulphate, adsorbed forms, oxide coatings and crystalline sediments (Carson 1981). According to inorganic models, the major dissolved species of cobalt in aerobic (normally oxygenated) fresh water at pH 8.0 are the free ion (~45%) and the carbonate (~45%). Adsorbed forms account for approximately 8% (Sibley and Morgan 1975). Cobalt forms very stable complexes with such compounds as EDTA and NTA; the chelation of cobalt to such multidentate ligands strongly enhances its solubility and mobility in aqueous systems. Inorganic models have shown that cobalt is present as the aquated cobaltous ion and the EDTA complex in water at pH 7 containing silica. Concentrations of EDTA more than 20 times the total cobalt concentration alter the speciation of cobalt such that complexed soluble forms predominate (Vuceta and Morgan 1978). Organic pollution appears to sometimes enhance the solubility of cobalt in fresh water, by complexing it with sewage-derived organic compounds (Smith and Carson 1981).

Cobalt may be removed from the water column by adsorption to suspended particulates and sediment materials. Cobalt, at concentrations ranging from 50 to 200 $\mu g \cdot L^{-1}$ in artificial river water at pH 8, was 95% adsorbed by 1000 $mg \cdot L^{-1}$ illite suspensions. At pH 4, 20% adsorption occurred. By increasing calcium ion concentration from 1.5 to 15 $mg \cdot L^{-1}$ at pH 4, adsorption was reduced to 10% (O'Connor and Kester 1975). In laboratory experiments, 90% of the cobalt was adsorbed by montmorillonite and illite (Kharkar *et al.* 1968). At a cobalt concentration of 5.9 $\mu g \cdot L^{-1}$ in aerobic fresh water, model calculations have predicted that adsorption to silica, ferric oxide and manganese oxide amounted to less than 2% of the total cobalt concentration (Vuceta and Morgan 1978).

Cobalt distribution in natural sediments is frequently related to that of fine grain material, which is usually dominated by clay minerals (Schrader *et al.* 1977). Whereas 40% of the cobalt found in sediments from the lower reaches of the Yamaska and St. François rivers in Quebec was bound to iron and manganese oxides, more than 50% was found in the fraction containing detrital silicate minerals, resistant sulphides and small amounts of organic substances resistant to acidic peroxide treatment (Tessier *et al.* 1979). Cobalt in suspended sediment of the Redstone River, in the Mackenzie Valley, was leached faster and to a greater extent by 0.1 M HCl (12-49%) than by EDTA (2.1-17%), indicating that inorganic species seemed to predominate over organic substances in these sediments (Wagemann *et al.* 1977). Adsorption to clay minerals is influenced by pH; it is low at low pH, but approaches 100% when the pH is increased (~ pH 7-10) so that hydrolysis of cobalt becomes significant (Carson 1981). In Var River (Monaco) water at a sediment load of 250 $mg \cdot kg^{-1}$ and cobalt concentration of 25 $\mu g \cdot L^{-1}$, sorption increased from approximately 0% at pH 4 to about 35% at pH 7.5. At pH 8, sorption increased to 100% (Murray and Murray 1973).

Organic compounds in water may cause desorption and solubilization of cobalt from inorganic fractions of sediment (Carson 1981). For example, in the Var River, the concentration of soluble cobalt increased as the amount of soluble organic matter increased. At pH 8.1, in the absence of sewage, cobalt was 93% sorbed to sediment. With increasing sewage loads, cobalt sorption decreased from 87% at 25% sewage load to 64% at 100% sewage load (Murray and Meinke 1974).

Some aquatic organisms may readily accumulate cobalt to levels several orders of magnitude above those found in the water column. Freshwater algae may attain concentration factors between 400 and 2 x 10^6, although it is not clear whether this is because of actual biological uptake or physical adsorption. Submerged or floating aquatic plants which obtain nutrients directly from the water may attain concentration factors as high as those of algae. Rooted freshwater plants generally have concentration factors below 10. Benthic organisms have higher concentration factors than do surface organisms, and sessile organisms generally have higher concentration factors than do free-swimming organisms. Freshwater molluscs have concentration factors between 100 and 14 000, whereas oligochaetes have concentration factors of approximately 30. Insects and insect larvae may often have very high levels of cobalt, with concentration factors as high as 10^6. Other invertebrates, such as Hirudinea and Crustacea, attain concentration factors between 1 and 11 000. Because concentration factors generally decrease with increasing trophic status, biomagnification is not considered to be significant (Cole and Carson 1981).

6.2.15.5 References

Benoit, R.J. 1957. Preliminary observations on cobalt and vitamin B_{12} in freshwater. Limnol. Oceanogr. 2: 233-240.

Carson, B.L. 1981. Environmental transport. *In* Trace Metals in the Environment. Vol. 6. Cobalt. I.C. Smith and B.L. Carson (eds.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 531-662.

Cole, C.J. and B.L. Carson. 1981. Cobalt in the food chain. *In* Trace Metals in the Environment. Vol. 6. Cobalt. I.C. Smith and B.L. Carson (eds.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 777-924.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Kharkar, D.P., K.K. Turekian and K.K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. Geochim. Cosmochim. Acta 32: 285-298.

Murray, C.N. and S. Meinke. 1974. Influence of soluble sewage material on adsorption and desorption behavior of cadmium, cobalt, silver and zinc in sediment-freshwater, sediment-seawater systems. Nippon Kaiyo Gakkai-Shi 30: 216-221.

Murray, C.N. and L. Murray. 1973. Adsorption-desorption equilibria of some radionuclides in sediment-freshwater and sediment-seawater systems. *In* Symp. on the Interaction of Radioactive Contaminants with the Constituents of the Marine Environment, July 10-14, 1972. Int. Atomic Energy Agency, Pap. No. IAEA/SM-158/7. Seattle, Washington. p. 26.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

O'Connor, T.P. and D.R. Kester. 1975. Adsorption of copper and cobalt from fresh and marine systems. Geochim. Cosmochim. Acta 39: 1531-1543.

Parker, M. and A.D. Hasler. 1969. Studies on the distribution of cobalt in lakes. Limnol. Oceanogr. 14: 229-241.

Schrader, E.L., Jr., J.H. Rule and W.J. Furbish. 1977. Trace metal geochemistry of a fluvial system in eastern Tennessee affected by coal mining. Southeast. Geol. 18: 157-172.

Sibley, T.H. and J.J. Morgan. 1975. Equilibrium speciation of trace metals in freshwater: seawater mixtures. *In* Int. Conf. on Heavy Metals in the Environment. Vol. 1. Institute of Environmental Studies, University of Toronto, Toronto, Ontario. pp. 319-338.

Smith, I.C. and B.L. Carson (eds.). 1981. Trace Metals in the Environment. Vol. 6. Cobalt. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan.

Telewiak, R.G. 1985. Cobalt. *In* Canadian Minerals Yearbook. 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 21.1-21.5.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844-851.

Trisdan, G.M., R.R. Wilkinson and B.L. Carson. 1981. Chemistry. *In* Trace Metals in the Environment. Vol. 6. Cobalt. I.C. Smith and B.L. Carson (eds.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 229-370.

Vuceta, J. and J.J. Morgan. 1978. Chemical modeling of trace metals in fresh waters: role of complexation and adsorption. Environ. Sci. Technol. 12: 1302-1309.

Wagemann, R., G.J. Brunskill and B.W. Graham. 1977. Composition and reactivity of some river sediments from the Mackenzie Valley, NWT, Canada. Environ. Geol. 1: 349-358.

Wetzel, R.G. 1975. Limnology. W.B. Saunders & Co., Philadelphia, Pennsylvania. 743 pp.

Young, R.S. 1979. Cobalt in Biology and Biochemistry. Academic Press, London. 147 pp.

6.2.16 Copper

6.2.16.1 Uses and Production

Copper metal and copper compounds have been used by humans since prehistoric times. Copper's usefulness as a metal is estimated as being second only to that of iron (Demayo and Taylor 1981). Modern uses of copper include electrical wiring and electroplating, the production of alloys (e.g. bronze and brass), photography, utensils, antifouling paint, art designs, pesticide formulations and textiles. Copper is also used in construction, in roofing materials and brass and copper plumbing (Demayo and Taylor 1981; Windholtz *et al.* 1983).

The 1981 Canadian mine production of copper was 691 400 t which was 8.3% of world mine production. Canada was the fourth largest mine producer after the United States (18.5% of world production), U.S.S.R. (13.7%) and Chile (13.0%). In Canada, copper mine production is concentrated in four provinces: British Columbia (41.7%), Ontario (32.7%), Quebec (13.0%) and Manitoba (8.1%). Copper smelters are located in Ontario, Quebec and Manitoba, and refineries are found in Ontario and Quebec. Canada exports most of the copper produced as copper ores, concentrates and matte, as well as copper refinery shapes. Canadian production of refined copper in 1981 was 476 600 t, or about 5.0% of world production (Cranstone 1984).

6.2.16.2 Sources and Pathways for Entering the Aquatic Environment

Copper is a common metallic element in the rocks and minerals of the earth's crust. It is sometimes found in a pure state as native copper, but normally copper occurs in the form of mineral ores which contain 2% or less of the metal. More than 160 copper-containing minerals have been described, with sulphides, oxides and carbonates comprising the principal copper ores. Chalcopyrite ($CuFeS_2$) is by far the most abundant of the copper minerals, probably accounting for about 50% of the world's copper deposits. Copper is also often found in association with other metals and metalloids, including iron, nickel, zinc, arsenic, antimony, bismuth, molybdenum, silver, gold and platinum (Massey 1973).

Natural sources of copper in aquatic environments include the weathering or the solution of copper minerals and native copper. Anthropogenic activities can, however, release significant amounts of copper to the environment (McNeely *et al.* 1979). It is estimated that anthropogenic sources of copper to aquatic environments represent 33-60% of the total annual global input (Demayo and Taylor 1981). These sources include corrosion of brass and copper pipe by acidic waters; sewage treatment plant effluents; the use of copper compounds as aquatic algicides; runoff and groundwater contamination from agricultural uses of copper as fungicides and pesticides in the treatment of soils; and effluents and atmospheric fallout from industrial sources. Major industrial sources include mining, smelting and refining industries; copper wire mills; coal-burning industries; and iron- and steel-producing industries (U.S. EPA 1980; Demayo and Taylor 1981).

6.2.16.3 Environmental Concentrations

Copper ranks 25th in abundance among the elements in the earth's crust (Taylor 1964). The average concentration of copper in crustal (igneous) rocks (23.6-55 $mg{\cdot}kg^{-1}$) (Cox 1979) is higher than the average concentration in sedimentary rocks (4-45 $mg{\cdot}kg^{-1}$) (Turekian and Wedepohl 1961; Bowen 1966; Krauskopf 1972). Copper is more common in the earth's crust than are other well-known elements, such as cobalt or lead, but less common than zinc, nickel and chromium (Demayo and Taylor 1981).

Background concentrations of copper in surface waters are usually well below 20 $\mu g{\cdot}L^{-1}$. Higher concentrations are generally related to anthropogenic sources (McNeely *et al.* 1979; U.S. EPA 1980). Dissolved total copper levels in Canadian surface waters rarely exceed 5 $\mu g{\cdot}L^{-1}$ (Spear and Pierce 1979), whereas concentrations of 1-10 $\mu g{\cdot}L^{-1}$ are commonly reported for unpolluted surface waters in the United States

Table 6-13. Environmental Concentration Ranges for Total Copper in Canadian Surface Waters

Region	Concentration range[1] ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	1-80	158	1981-1982
Western	1-71	368	1980-1983
Central	1-68	1333	1981-1983
Atlantic	2-70	232	1980

[1] Detection limit is 1 $\mu g \cdot L^{-1}$.

Source: NAQUADAT 1985.

(U.S. EPA 1980). The levels of dissolved copper in the freshwater-saltwater mixing zones of estuaries may be higher than those in the inflowing river waters (DeGroot and Allersma 1975; Thomas and Grill 1977). This is presumably a result of desorption caused by the increased salinity (ionic strength) (Sibley and Morgan 1975) and bacterial decomposition of organic matter (DeGroot and Allersma 1975).

The average copper concentration in Canadian tap water was 65 $\mu g \cdot L^{-1}$, based on 276 NAQUADAT stations. Forty-four percent of the stations reported concentrations below 10 $\mu g \cdot L^{-1}$, and 10% had concentrations greater than 180 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1980).

Mean copper concentrations for Canadian freshwater sediments ranged from 12 to 57 $\mu g \cdot g^{-1}$, with individual values as high as 4000 $\mu g \cdot g^{-1}$ (Spear and Pierce 1979).

Concentration ranges for copper in Canadian surface waters between 1980 and 1983 are presented in Table 6-13.

6.2.16.4 Forms and Fate in the Aquatic Environment

Copper occurs in four oxidation states, 0, +1, +2 and +3; the two most common are +1 (cuprous) and +2 (cupric). Cuprous copper (Cu(I)) is unstable in aerated aqueous solutions, and will normally be oxidized to cupric copper (Cu(II)) (Garrels and Christ 1965; Massey 1973). Copper exhibits complex behaviour in the aquatic environment; attempts to quantitate its chemical speciation in aqueous systems have yielded conflicting conclusions, mainly because of uncertainties in such thermodynamic data as hydrolysis and complex formation equilibria constants and solubilities, and in adsorption characteristics (Leckie and Davis 1979). Copper may be present in solution as cupric ions or complexed with inorganic or organic ligands. It may also be associated with suspended or bed sediments, or be present as precipitates of hydroxides, phosphates and sulphides or sorbed to surfaces (Stiff 1971). The composition of the various copper species depends on pH and on the presence of other inorganic and organic ligands in water. Copper is generally more soluble in acidic waters, and precipitates as $Cu(OH)_2$ at pH values above 6.5. Generally, divalent copper salts are very soluble in water. In the presence of excess cupric ion in alkaline waters, carbonates, hydroxides, oxides and sulphides will form colloidal suspensions or will precipitate out of solution. At pH levels and inorganic carbon concentrations characteristic of natural fresh waters, most of the soluble copper is present as complexes of cupric carbonate (Stiff 1971). Less than 1% of the total copper exists in the free ionic form in natural water (Alabaster and Lloyd 1982).

Sorption and precipitation play major roles in determining the abiotic fate of copper in the aquatic environment. Copper has a high affinity for hydrous iron and manganese oxides, clays, carbonate minerals and organic matter. In reducing acidic environments, remobilization of sorbed or coprecipitated copper can occur (Lee 1975; Huang *et al.* 1977). In the presence of soluble organic matter, sorption of copper may be relatively ineffective, resulting in an increase in soluble forms in the water column (Jackson and Skippen 1978; U.S. EPA 1979).

Although some copper complexes are photosensitive, there is no evidence to suggest that photolysis plays a significant role in copper dynamics in the aquatic environment. Likewise, volatilization is considered to be insignificant (U.S. EPA 1979).

As an essential element, copper is readily accumulated by plants and animals; bioconcentration factors ranging from 100 to 26 000 have been recorded for various species of phytoplankton, zooplankton, macrophytes, macroinvertebrates and fish (Spear and Pierce 1979). However, whole-body concentrations tend to decrease with increasing trophic level, presumably because of organ-specific accumulation and metabolic regulation in most consuming organisms. It is believed that copper is not biomagnified to any significant extent (Hutchinson *et al.* 1976).

6.2.16.5 References

Alabaster, J.S. and R. Lloyd. 1982. Water Quality Criteria for Freshwater Fish. 2nd edition. Butterworth Scientific, London. 361 pp.

Bowen, H.J.M. 1966. Trace Elements in Biochemistry. Academic Press, New York. (Cited in Demayo and Taylor 1981.)

Cox, D.P. 1979. The distribution of copper in common rocks and ore deposits. *In* Copper in the Environment. Part 1: Ecological Cycling. J.O. Nriagu (ed.). John Wiley & Sons, Toronto, Ontario. pp. 19-42.

Cranstone, D. 1984. Copper. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report 32.

DeGroot, A.J. and E. Allersma. 1975. Field observations on the transport of heavy metals in sediments. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Toronto, Ontario. pp. 85-96.

Demayo, A. and M.C. Taylor. 1981. Copper. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Garrels, R.M. and C.L. Christ. 1965. Solutions, Minerals and Equilibria. Harper & Row, New York. (Cited in U.S. EPA 1980.)

Health and Welfare Canada. 1980. Copper. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 209-277.

Huang, C.P., H.A. Elliot and R.M. Ashmead. 1977. Interfacial reactions and the fate of heavy metals in soil-water systems. J. Water Pollut. Control Fed. 49: 745-756.

Hutchinson, T.C., A. Fedorenko, J. Fitchko, A. Kuja, J. VanLoon and J. Lichwa. 1976. Movement and compartmentation of nickel and copper in an aquatic ecosystem. *In* Proc. Int. Symp. on Environmental Biogeochemistry. J.O. Nriagu (ed.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 565-585.

Jackson, K.S. and G.B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: a laboratory study of copper, lead, zinc and nickel behaviour at a simulated sediment-water boundary. J. Geochem. Explor. 10: 117-138.

Krauskopf, K.B. 1972. Geochemistry of micronutrients. *In* Micronutrients in Agriculture. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (eds.). Soil Science Society of America, Inc. Madison, Wisconsin. pp. 7-40. (Cited in U.S. EPA 1979.)

Leckie, J.O. and J.A. Davis. 1979. Aqueous environmental chemistry of copper. *In* Copper in the Environment. Part 1: Ecological Cycling. J.O. Nriagu (ed.). John Wiley & Sons, Toronto, Ontario. pp. 89-121.

Lee, G.F. 1975. Transport of heavy metals in the environment. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Oxford. pp. 137-147.

Massey, A.G. 1973. Copper. *In* Comprehensive Inorganic Chemistry. Vol. 3. J.C. Bailar, Jr., H.J. Emeléus, Sir R. Nyholm and A.F. Trotman-Dickenson (eds.). Pergamon Press, Toronto, Ontario. pp. 1-78.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Copper. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 14-15.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Sibley, T.H. and J.J. Morgan. 1975. Equilibrium speciation of trace metals in freshwater:saltwater mixtures. *In* Int. Conf. on Heavy Metals in the Environment. Vol. I. October 27-31, Toronto, Ontario. pp. 319-338.

Spear, P.A. and R.C. Pierce. 1979. Copper in the Aquatic Environment: Chemistry, Distribution and Toxicology. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16454. 227 pp.

Stiff, M.J. 1971. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. Water Res. 5: 585-599.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285. (Cited in Demayo and Taylor 1981.)

Thomas, D.J. and E.V. Grill. 1977. The effect of exchange reactions between Fraser River sediment and seawater on dissolved copper and zinc concentrations in the Strait of Georgia. Estuarine Coastal Mar. Sci. 5: 421-427.

Turekian, K.K. and K.H. Wedepohl. 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72: 175-192. (Cited in Demayo and Taylor 1981.)

U.S. EPA. 1979. Copper. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 11-1 to 11-19.

U.S. EPA. 1980. Ambient Water Quality Criteria for Copper. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-036.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck & Co., Inc., Rahway, New Jersey.

6.2.17 Cyanides

6.2.17.1 Uses and Production

In Canada, the primary users of organic cyanide compounds (nitriles) are industries involved in the production of acrylonitrile, adiponitrile and methylmethacrylate. Sodium cyanide is used in the extraction of gold and silver from low-grade ores, in steel production, in electroplating and as an intermediate for chemical syntheses. Some compounds containing cyanide may also be used as pesticides (Health and Welfare Canada 1980; Leduc *et al.* 1982).

Data on the quantity of cyanide produced in Canada are not readily available (Health and Welfare Canada 1980). In 1974, Canadian consumption was 258.6 t of which 75% was consumed in Ontario and 20% in Quebec (Environment Canada 1975). In the U.S.A., cyanide production in 1978 was more than 315 000 t. Importation information on cyanide compounds for 1981 and 1982 is presented in Table 6-14.

Table 6-14. Importation of Cyanide Compounds into Canada

	Amount (t)	
Compound	1981	1982
Calcium cyanide (fumigants)	1	—
Sodium cyanide	5520	7078
Copper cyanide	127	50
Potassium cyanide	130	68
Zinc cyanide	47	16
Potassium ferricyanide	51	20
Metallic cyanides (not specified inorganic)	11	3
Metallic cyanides (complex, inorganic)	425	391

Source: Statistics Canada 1983.

6.2.17.2 Sources and Pathways for Entering the Aquatic Environment

In Canada, cyanides are released into the aquatic environment from effluents of gold mining and milling industries (Conn 1981; Leduc *et al.* 1982). Cyanide concentrations in the final effluent of six Canadian gold mills were 0.3-26.5 $\mathrm{mg \cdot L^{-1}}$ total cyanide. Cyanides also enter the aquatic environment through waste effluents from industrial processes, such as gas works, coke ovens, gas scrubbing in steel plants, metal cleaning and electroplating (McNeely *et al.* 1979). Concentrations ranging from 30 to 60 $\mathrm{mg \cdot L^{-1}}$ were found in steel mill effluents; from 2 to 4 $\mathrm{mg \cdot L^{-1}}$ in oil refinery effluents; and an average of 3 $\mathrm{mg \cdot L^{-1}}$ was found in effluents from electroplating industries. In addition, small amounts of cyanides may be discharged into the environment from burning certain synthetic and natural materials, from chemical, biological and clinical laboratories and from the application of chemicals containing cyanides on land and water (Leduc *et al.* 1982).

Cyanides may also be released into the aquatic environment through the decomposition of plants that synthesize cyanoglycosides and microorganisms that produce free cyanide as a result of their metabolic processes. The snow mold fungus (an unidentified basidiomycete), the blue-green alga *Anacystis nidulans* and the bacterium *Cromobacterium violaceum* produce HCN in laboratory cultures. Some foods of plant origin have high cyanide content, e.g. bitter almonds, lima beans and cassava (Health and Welfare Canada 1980; Leduc *et al.* 1982).

6.2.17.3 Environmental Concentrations

Cyanides are found generally in small concentrations in surface waters, as a result of both natural and anthropogenic inputs (Leduc *et al.* 1982). Cyanide, expressed as total cyanide, has been measured in surface waters in rural and wilderness areas in Canada. Concentrations as high as 30-60 $\mathrm{\mu g \cdot L^{-1}}$ have been reported (Leduc *et al.* 1982). A survey, carried out between 1974 and 1977 on 11 rivers from western and central Canada, showed that concentrations of cyanide varied considerably with river size. In small and medium rivers, peak concentrations were more frequent in the fall and winter during minimal runoff; in larger rivers, peak cyanide concentrations occurred during and after the May-June runoff period (Leduc *et al.* 1982).

Samples from the Ottawa River indicate concentrations of cyanide below 10 $\mu g \cdot L^{-1}$ for both raw and treated water. In Manitoba, 116 of 124 water sampling stations reported concentrations of cyanide in treated water to be less than 100 $\mu g \cdot L^{-1}$, with a median value of 30 $\mu g \cdot L^{-1}$ (Health and Welfare Canada 1980). From 1965 to 1976 in British Columbia, the concentrations of total cyanide (90th percentile) for streams (1849 measurements), lakes (361 measurements) and marine waters (22 measurements) were 10, 40 and <10 $\mu g \cdot L^{-1}$, respectively. The minimum detectable concentration for cyanide during this period was 10 $\mu g \cdot L^{-1}$ (Clark 1978).

Environmental concentration ranges for cyanide in Canadian surface water are presented in Table 6-15.

6.2.17.4 Forms and Fate in the Aquatic Environment

Cyanides comprise a diverse group of organic and inorganic compounds characterized by the $-C\equiv N$ group. The form of cyanide in water is dependent primarily on pH, but is also influenced to a lesser degree by temperature, dissolved oxygen, salinity and the presence of other ions, complexing agents and sunlight (U.S. EPA 1979; Leduc *et al.* 1982).

Cyanide compounds may be grouped according to their physical and chemical properties as free, simple, complex and organic cyanides (Kelada *et al.* 1976). Cyanide ion refers to the single, free anion (CN^-), excluding all other cyanide species (Doudoroff 1976). Molecular HCN (hydrocyanic acid, hydrogen cyanide) refers to cyanide in the form of an uncharged, undissociated molecule. Free cyanide refers to the summation of molecular HCN and the cyanide ion in aqueous solution, irrespective of their sources in water. Simple cyanides are those compounds that dissociate directly in water to yield a cation and the cyanide ion, with no soluble intermediates. Complex cyanide may dissociate in water to a cation and an anion composed of two or more different chemical forms, one of which is cyanide. The anion is termed a complex ion and may be subject to further dissociation, possibly releasing free cyanide ions (Ecological Analysts 1979).

Organic compounds containing the group $-C\equiv N$ are termed nitriles or cyanides, depending upon the nomenclature used (IUPAC 1979). Cyanates are compounds containing the $-OCN$ group; aqueous solutions hydrolyze to ammonia and the corresponding bicarbonate (Towill *et al.* 1978). Cyanates are relatively stable at pH 7 in aerobic water at 20°C for up to 10 d; decomposition may accelerate, however, at lower pH. Thiocyanates, compounds containing the $-SCN$ group, are more stable than cyanates, and form complexes with numerous elements (Cotton and Wilkinson 1980). Alkali and alkaline earth thiocyanates are usually readily soluble, and appear to be stable in aqueous solutions (Kelada *et al.* 1976).

The term "total cyanide" has been used in the literature to convey different ideas (Doudoroff 1976). From an operational viewpoint, total cyanide comprises all cyanide and some cyanate species or groups determinable by a particular, selected analytical method (Leduc *et al.* 1982). Total cyanide also refers to the summation of the CN group in all the different forms of cyanide that exist in aqueous solution. Terms such as "total cyanide", "oxidizable cyanide", "cyanide amenable to chlorination" and "cyanide amenable to ozonation" reflect the corresponding methods of analysis (IUPAC 1979).

Table 6-15. Environmental Concentration Ranges for Cyanide in Canadian Surface Waters

Region	Concentration range[1] ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[2,3]-9.7	147	1980-1983
Western	<2-2.1	33	Prior to 1980
Central	<2-370	134	1980-1983

[1] Detection limit is ~2 $\mu g \cdot L^{-1}$ (total).
[2] Detection limit is 0.5 $\mu g \cdot L^{-1}$.
[3] ND = not detected.

Source: NAQUADAT 1985.

With respect to free cyanide in aqueous systems, an equilibrium is rapidly established between molecular cyanide and cyanide ion. This equilibrium is dependent primarily upon pH and, to a lesser degree, temperature. For example, at 10°C and pH 6.0, more than 99% of the cyanide present exists as HCN. The proportion of HCN decreases to 92% at pH 8.5 and 10°C. At 4°C and pH 8.5, the proportion of HCN is 94%. Hence, under typical environmental conditions, most of the free cyanide would be present as HCN (Sharpe 1976).

Simple cyanides, such as alkali cyanides, readily dissociate in water to yield the cyanide ion, which then enters into equilibrium with HCN. It has been observed that there are 28 elements that may form complex cyanide compounds, and there are more than 68 oxidation states of these elements capable of forming complex cyanides (Broderius 1973). Hence, there exists the possibility of a multitude of complex metallocyanides that may occur in aqueous systems, each possessing unique physical and chemical properties. Little information is available on the predominant chemical species of complex cyanides present in the Canadian aquatic environment (Leduc *et al.* 1982).

Some complex metallocyanides may dissociate in water, generating complex cyanide ions which may further dissociate, releasing free cyanide ion. In general, many complex ions are more stable than their parent compounds, and, hence, subsequent dissociation to cyanide ions may be relatively minor. Depending upon the chemical species, some complex cyanide ions may, however, readily dissociate. The degree of dissociation to form cyanide ion is, in general, dependent upon pH and light intensity. Iron-cyanide complex ions may dissociate to cyanide ions in the presence of sunlight below about pH 8 (Leduc *et al.* 1982).

Most of the information regarding the fate of cyanides in the aquatic environment has been derived from studies on the treatment of complex industrial wastes containing cyanides in the milligram per litre range, usually in association with other substances. Concentrations in wastewater were found to be lowered by such processes as chemical oxidation, irradiation, biodegradation, volatilization, photolysis, dissociation and precipitation (Leduc *et al.* 1982). It is, however, difficult and often misleading to extrapolate such information to natural conditions. From the limited information available under natural conditions, it cannot be assumed that cyanides have a short residence time in the aquatic environment (Leduc *et al.* 1982).

Hydrogen cyanide is volatile, having a vapour pressure of 53.1 kPa at 10.2°C (Schneider and Freund 1962). Volatilization is expected to be a significant removal process for free cyanide from concentrated solutions; information on volatilization from dilute solutions is, however, lacking (Leduc *et al.* 1982). Chemical oxidation is a commonly used treatment technique (Kunz *et al.* 1978); reliable data on the chemical oxidation of free cyanide in dilute solutions are not available. Cyanide ion is not strongly adsorbed and retained in soils (Broderius and Smith 1980). Numerous microorganisms have been identified which are capable of degrading free cyanide (Towill *et al.* 1978), and cyanides may be removed from waste streams by biological treatment (Kunz *et al.* 1978).

Little information is available on the fate of complex cyanides in natural waters. The role of precipitation and sorption in the removal of complex cyanides from the water column has not been adequately examined. Numerous metallocyanide complex ions are stable in aqueous solution in the absence of ultraviolet and visible light; in the presence of sunlight, however, photodecomposition of some complexes, with the resultant release of cyanide ions, may occur (Broderius and Smith 1980).

6.2.17.5 References

Broderius, S.J. 1973. Determination of Molecular Hydrocyanic Acid in Water and Studies on the Chemistry and Toxicity to Fish of Metal-Cyanide Complexes. Ph.D. Thesis, Oregon State University, Corvallis, Oregon. 287 pp.

Broderius, S.J. and L.L. Smith, Jr. 1980. Direct Photolysis of Hexacyanoferrate Complexes. Proposed Applications to the Aquatic Environment. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-80-003. 50 pp.

Clark, M.J.R. 1978. A Statistical Overview of Water Quality Analysis for British Columbia: 1965-1976. Rep. No. 78-4. Pollution Control Branch, British Columbia Ministry of the Environment, Victoria, B.C.

Conn, K. 1981. Cyanide analysis in mine effluents. Presented at Canadian Mineral Processors 13th Annual Meeting, January 20-22, 1981, Ottawa. (Cited in Leduc *et al.* 1982.)

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Doudoroff, P. 1976. Toxicity to Fish of Cyanides and Related Compounds. A Review. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-76-038. 154 pp.

Ecological Analysts. 1979. Cyanide. A Review and Analysis of the Literature on Chemistry, Fate, Toxicity and Detection in Surface Waters. Ecological Analysts, Towson, Maryland. 83 pp.

Environment Canada. 1975. Review of the Canadian Metal Finishing Industry: Consumption of Raw Materials and Options for Water Pollution Control. EPS 3-WP-75-2.

Health and Welfare Canada. 1980. Cyanide. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 279-285.

IUPAC (International Union of Pure and Applied Chemistry). 1979. Nomenclature of Organic Chemistry. Sections A, B, C, E, F and H. Pergamon Press, Oxford. pp. 269-271.

Kelada, N.P., D.T. Lordi and C. Hue-Hing. 1976. Cyanide species methodology in water, wastewater and sediments. *In* Advances in Automated Analysis. Technicon Int. Congr. Vol. 2. pp. 73-82.

Kunz, R.G., J.P. Casey and J.E. Huff. 1978. Refinery cyanides – a regulatory dilemma. Hydrocarbon Process. 57: 98-106.

Leduc, G., R.C. Pierce and I.R. McCracken. 1982. The Effects of Cyanides on Aquatic Organisms with Emphasis upon Freshwater Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC 19246. 139 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Cyanide. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 15-16.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Schneider, C.R. and H. Freund. 1962. Determination of low level hydrocyanic acid in solution using gas-liquid chromatography. Anal. Chem. 34: 69-74.

Sharpe, A.G. 1976. The Chemistry of Cyano Complexes of the Transition Metals. Academic Press, New York. 302 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Towill, L.E., J.S. Drury, B.C. Whitfield, E.B. Lewis, E.L. Galyan and A.S. Hammons. 1978. Reviews of Environmental Effects of Pollutants. V. Cyanide. Oak Ridge National Laboratory, Oak Ridge, Tennessee. ORNL/EIS-81. (EPA-600/1-78-027.) 190 pp.

U.S. EPA. 1979. Cyanide. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 12-1 to 12-12.

U.S. EPA. 1980. Ambient Water Quality Criteria for Cyanides. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-037.

6.2.18 Fluoride

6.2.18.1 Uses and Production

Fluorides are used in a variety of industrial processes, including metal plating, metal casting, welding, brazing and the manufacture of aluminum, steel, bricks, tiles, glass and ceramics, hydrofluoric acid and other fluorine chemicals, adhesives and metallurgical fluxes. Other uses include phosphate fertilizers, insecticides and herbicides and the refining of uranium ores. Fluoride is often added to domestic water supplies to reduce dental caries, and is also used in toothpaste, tooth powders, mouthwashes and vitamin supplements (Environment Canada 1976; McNeely *et al.* 1979; Health and Welfare Canada 1980; Ontario Ministry of the Environment 1981).

No production of fluoride takes place in Canada. The only fluorspar (mineral containing fluoride) mine in Canada at St. Lawrence, Newfoundland, produced 64 000 t of fluorspar concentrate in 1976, its last year of operation. This mine, however, is scheduled to reopen in 1986 (Boucher 1985). World production of fluorspar in 1978 was 4 792 000 t (Boyd 1982). World production of fluorine from fluorspar and phosphate rock in 1978 was 2 150 000 t (Morse 1980). Canadian production of hydrogen fluoride was 78 500 t in 1981, and 500 t were imported in the same year (CORPUS Information Services 1982). In 1981 and 1982, 7089 t and 7712 t, respectively, of fluorides and other fluoride salts were imported into Canada (Statistics Canada 1983).

6.2.18.2 Sources and Pathways for Entering the Aquatic Environment

Fluoride is present in trace amounts in soils and rocks, but is most prevalent in active or inactive volcanic regions (Environment Canada 1976). The weathering of alkaline and siliceous, igneous and sedimentary rocks, especially shales, supplies fluorides to the aquatic environment. The principal fluoride-containing minerals are fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5F(PO_4)_6$) (IJC 1977; McNeely *et al.* 1979).

The presence of fluoride in the aquatic environment is also a result of the addition of fluoride to domestic water supplies and resulting sewage discharge (McNeely *et al.* 1979). The average concentration of fluoride in 57 Ontario municipal sewage plants surveyed in 1976 was 1.0 $mg \cdot L^{-1}$ (Environment Canada 1978). Insecticides and herbicides containing fluorides may contribute fluoride to water (McNeely *et al.* 1979). An industrial wastewater sampling station in British Columbia was sampled three times in 1982 for fluoride (dissolved); the concentrations reported were 5.86, 8.84 and 9.88 $mg \cdot L^{-1}$ (NAQUADAT 1985).

Volcanic activity contributes fluorine-containing dusts and gases to the atmosphere, although most of the airborne fluoride is considered to be of industrial origin (Rose and Marier 1977; Health and Welfare Canada 1980). The primary aluminum reduction industry is the largest industrial source of atmospheric fluoride (56.5%) in Canada. The steel (15.5%) and phosphate (17.7%) industries are also major sources of fluoride to the atmosphere (Environment Canada 1976; Rose and Marier 1977). The combustion of coal introduces fluoride into the atmosphere; however, unless an industrial spillage occurs, large quantities are seldom discharged into the environment (McNeely *et al.* 1979). Filters, electrostatic precipitators and various wet-scrubbing systems can remove a substantial amount of fluoride in emissions (Rose and Marier 1977).

6.2.18.3 Environmental Concentrations

Fluoride is abundant in the earth's crust, and detectable concentrations occur in almost all minerals (IJC 1977; McNeely *et al.* 1979; Health and Welfare Canada 1980). The concentration of fluoride in most surface waters is less than 1 $mg \cdot L^{-1}$ (Livingstone 1963; Wetzel 1975; McNeely *et al.* 1979), although concentrations may exceed 50 $mg \cdot L^{-1}$ (McNeely *et al.* 1979). The highest natural concentrations, many exceeding 1000 $mg \cdot L^{-1}$, are found in the lakes of East Africa (Kilham and Hecky 1973). Many natural freshwater streams contain less than 0.2 $mg \cdot L^{-1}$ (Neuhold and Sigler 1960; Groth 1975; McNeely *et al.* 1979). Fluoride concentrations in the Great Lakes range from 0.05 to 0.14 $mg \cdot L^{-1}$ (IJC 1977). Groundwater usually contains higher concentrations than surface water, often as high as 10 $mg \cdot L^{-1}$ (McNeely *et al.* 1979). Environmental concentration ranges for fluoride in Canadian surface waters are presented in Table 6-16.

6.2.18.4 Forms and Fate in the Aquatic Environment

Fluorine, being the most reactive of the halogen series, does not occur free in nature, but is present as fluoride ion. In general, most fluorides associated with monovalent cations are water-soluble (e.g. NaF, AgF and KF), but those formed with divalent cations are usually insoluble (e.g. CaF_2 and PbF_2) (Cotton and Wilkinson 1980).

Fluoride is considered to be one of the main ions responsible for solubilizing beryllium, aluminum, scandium, niobium, tantalum, iron and tin in natural waters (Environment Canada 1976). Fluoride concentrations in inland lakes are believed to be regulated by the calcium-carbonate-phosphate-fluoride system, which may explain the observation of uniform fluoride concentrations at different depths (Kramer 1964).

Table 6-16. Environmental Concentration Ranges for Fluoride in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[2]-2.60	1408	1980-1985
Western	ND-0.74	3094	1980-1985
Central	0.0-2.0	2826	Prior to 1980
Atlantic	ND-0.29	2602	1980-1985

[1] Detection limit is 0.02 $mg \cdot L^{-1}$ (dissolved).
[2] ND = not detected.

Source: NAQUADAT 1985.

The presence of calcium in water limits fluoride toxicity. Fluorosis is less severe when the drinking water is hard rather than soft (Neuhold and Sigler 1960; Herbert and Shurben 1964). In addition, calcium and chloride reduce the toxic responses of fish to fluoride (Groth 1975a).

Numerous aquatic plants and animals may accumulate fluoride to concentrations that may be severalfold higher than those occurring in the water column. Both freshwater and marine algae and some vascular plants have been found to accumulate fluoride at concentrations 20-50 times ambient levels (Sigler and Neuhold 1972; Groth 1975a, b). Aquatic invertebrates readily accumulate fluoride, some having concentration factors of 100 (Stewart *et al.* 1974; Groth 1975a). Concentrations in the range of 10-100 $mg \cdot kg^{-1}$ (dry weight) have been found in the exoskeleton of several aquatic invertebrates (Groth 1975a). Fish may accumulate fluoride, particularly in their skeletons (Wright and Davison 1975). Concentrations in the range of 100-1000 $mg \cdot kg^{-1}$ (dry weight) have been reported (Groth 1975a). Fluoride may also be biomagnified in aquatic systems. For example, in an unpolluted area in New Zealand, fluoride concentrations of 31-209 $mg \cdot kg^{-1}$ were found in the shells of invertebrates feeding on plankton. Fluoride concentrations of 1425-1882 $mg \cdot kg^{-1}$ were found in the skeletons of blue cod that fed on crab, shrimp and shellfish, indicating a biomagnification factor of at least an order of magnitude (Stewart *et al.* 1974).

6.2.18.5 References

Boucher, M. 1985. Personal communication. Mineral Policy Sector, Energy, Mines and Resources Canada, Ottawa.

Boyd, B.W. 1982. Fluorspar. *In* Canadian Minerals Yearbook 1980. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 191-196.

CORPUS Information Services. 1982. Hydrogen Fluoride. CPI Product Profiles. Don Mills, Ontario.

Cotton, P.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, Inc., Toronto, Ontario. 1396 pp.

Environment Canada. 1976. National Inventory of Sources and Emissions of Fluoride (1972). Environmental Protection Service, Ottawa. Rep. APCD 75-7.

Environment Canada. 1978. Sources of Metals and Metal Levels in Municipal Wastewaters. Res. Rep. No. 80. Environmental Protection Service, Ottawa. pp. 320-343.

Groth, E. 1975a. An evaluation of the potential for ecological damage by chronic low-level environmental pollution by fluoride. Fluoride 8: 224-240.

Groth, E. 1975b. Fluoride pollution. Environment 17: 29-38.

Health and Welfare Canada. 1980. Fluoride. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 287-306.

Herbert, D.W.M. and D.S. Shurben. 1964. The toxicity of fluoride to rainbow trout. Water Waste Treat. J. 10: 141-142.

IJC. 1977. Fluoride. *In* New and Revised Great Lakes Water Quality Objectives. Vol. II. Report to the Governments of the United States and Canada, International Joint Commission, Windsor, Ontario. pp. 94-104.

Kilham, P. and R.E. Hecky. 1973. Fluoride: geochemical and ecological significance in East African waters and sediments. Limnol. Oceanogr. 18: 932-945.

Kramer, J.R. 1964. Theoretical model for the chemical composition of fresh water with application to the Great Lakes. *In* Proc. 7th Conf. Great Lakes Research, April 6-7, Toronto, Ontario. pp. 47-160.

Livingstone, D.A. 1963. Data of Geochemistry. 6th edition. Chapter of Chemical Composition of Rivers and Lakes. U.S. Geol. Surv. Prof. Pap. 440-G. 64 pp. (Cited in Wetzel 1975.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Fluoride. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 17-18.

Morse, D.E. 1980. Fluorine. *In* Mineral Facts and Problems. U.S. Department of the Interior, Bureau of Mines, Washington, D.C. p. 307.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Neuhold, J.M. and W.F. Sigler. 1960. Effects of sodium fluoride on carp and rainbow trout. Trans. Am. Fish. Soc. 89: 358-370. (Cited in IJC 1977.)

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Rose, D. and J.R. Marier. 1977. Environmental Fluoride 1977. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16081. 151 pp.

Sigler, W.F. and J.M. Neuhold. 1972. Fluoride intoxication in fish: a review. J. Wildlife Dis. 8: 252-254.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Stewart, D.J., T.R. Manley, D.A. White, D.L. Harrison and E.A. Stringer. 1974. Natural fluoride levels in Bluff area, New Zealand. I. Concentrations in wildlife and domestic animals. N. Z. J. Sci. 17: 105-113.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

Wright, D.A. and A.W. Davison. 1975. The accumulation of fluoride by marine and intertidal animals. Environ. Pollut. 8: 1-13.

6.2.19 Hardness

6.2.19.1 Introduction

The term "hardness" is frequently used as an assessment of the quality of water. Hardness varies considerably according to local environmental conditions and anthropomorphic influences. Incrustation and excessive soap consumption are the main concerns with hardness. On heating, hard waters have a tendency to form scale deposits; soft water, on the other hand, may result in corrosion of water pipes (Health and Welfare Canada 1980).

Table 6-17. Hardness of Fresh Water

Hardness, concentration as calcium carbonate ($mg \cdot L^{-1}$)	Degree of hardness
0-30	Very soft
31-60	Soft
61-120	Moderately soft (hard)
121-180	Hard
180 and over	Very hard

Source: Thomas 1953.

Hardness is an important modifying factor in water quality in the sense that it can significantly influence the form and, hence, toxicity of numerous heavy metals (Stumm and Morgan 1970; Alabaster and Lloyd 1982).

6.2.19.2 Sources and Pathways for Entering the Aquatic Environment

Natural sources of hardness are primarily leaching of limestone formations, seepage and runoff from soils. Typically, water in areas containing carbonate rock is characteristically hard, whereas water draining igneous rocks is soft. Aluminum silicates, $CaCO_3$, $CaMg(CO_3)_2$ and other minerals are dissolved from sedimentary rocks by CO_2-enriched groundwater (Stumm and Morgan 1970). Industrial and industrially related sources of water hardness include the inorganic chemical industry and discharges from operating and abandoned mines (Health and Welfare Canada 1980). Industrial wastewater sampled from a NAQUADAT station in British Columbia had a maximum hardness range of 226-454 $mg \cdot L^{-1}$ $CaCO_3$ for five samples taken during the period between 1980 and 1981 (NAQUADAT 1985).

6.2.19.3 Environmental Concentrations

The degree of hardness is expressed numerically by several different scales which are in use in different countries (Wetzel 1975). One such scale is given and presented in Table 6-17.

The upper Great Lakes had hardness values ranging from 40 to 80 $mg \cdot L^{-1}$ (IJC 1976). Ontario lakes and streams ranged from 2 to 1803 $mg \cdot L^{-1}$, but most levels were between 40 and 200 $mg \cdot L^{-1}$ (Ontario Ministry of the Environment 1974). New Brunswick had hardness levels ranging from 5 to 300 $mg \cdot L^{-1}$ as $CaCO_3$. Environmental concentration ranges for hardness in Canadian surface waters are presented in Table 6-18.

Municipal water supplies in Canada showed that half of all Canadian municipalities had hardness levels below 80 $mg \cdot L^{-1}$, and 20% had levels above 180 $mg \cdot L^{-1}$ (Neri *et al.* 1972). In a recent survey of 525 municipalities throughout Canada, only 17 cities had drinking water hardness levels above 500 $mg \cdot L^{-1}$; these cities were in Ontario and Saskatchewan (Health and Welfare Canada 1980).

6.2.19.4 Forms and Fate in the Aquatic Environment

Water hardness is a measure of cations, predominantly divalent cations, dissolved in water. It is caused by metal cations, such as calcium, magnesium, strontium, barium and

Table 6-18. Environmental Concentration Ranges for Hardness in Canadian Surface Waters

Region	$CaCO_3$ concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	12.6-236.0	1549	1980-1985
Central	2.1-280.2	2079	1980-1985
Atlantic	3.0-28.2	78	1980-1985

[1] Detection limit is 1 mg·L^{-1} $CaCO_3$.

Source: NAQUADAT 1985.

manganous, ferrous and aluminum ions, in solution. These cations are associated with a number of anions in solution, principally carbonate, bicarbonate, sulphate, chloride and silicate (Marier *et al.* 1979). Calcium and magnesium are considered the primary contributors to hardness in natural waters (Stumm and Morgan 1970; Loewenthal and Marais 1976). Historically, water hardness has been related to water's capacity to produce lather from soap: the harder the water, the more difficult it is to lather soap.

Total hardness of fresh water is normally expressed as an equivalent of calcium carbonate. That part of the total hardness that is chemically associated with carbonate and bicarbonate anions in water is referred to as carbonate or temporary hardness in relation to municipal water supplies, as it can be removed by boiling. The amount of hardness in excess of the carbonate hardness is referred to as noncarbonate or permanent hardness, as it cannot be removed by boiling. Noncarbonate hardness is attributable to the association of hardness-causing cations with anions, such as sulphate, chloride and nitrate (Stumm and Morgan 1970; Loewenthal and Marais 1976).

6.2.19.5 References

Alabaster, J.S. and R. Lloyd. 1982. Water Quality Criteria for Freshwater Fish. 2nd edition. Butterworth Scientific, London, U.K. 361 pp.

Health and Welfare Canada. 1980. Hardness. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 307-316.

IJC. 1976. The Waters of Lake Huron and Lake Superior. Vol. 1. Summary and Recommendations. A Report by the Upper Lakes Reference Group, International Joint Commission, Windsor, Ontario.

Loewenthal, R.E. and G.V.R. Marais. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Application. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 433 pp.

Marier, J.R., L.C. Neri and T.W. Anderson. 1979. Water Hardness, Human Health and the Importance of Magnesium. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 17581. 119 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Neri, L.C., D. Hewitt and J.S. Mandel. 1972. Relation between mortality and water hardness in Canada. Lancet 1: 931. (Cited in Health and Welfare Canada 1980.)

Ontario Ministry of the Environment. 1974. Guidelines and Criteria for Water Quality Management in Ontario. Water Resources Branch, Toronto, Ontario.

Stumm, W. and J.J. Morgan. 1970. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience Publ., John Wiley & Sons, New York. 780 pp.

Thomas, J.F.J. 1953. Industrial Water Resources of Canada. Scope, Procedures and Interpretation of Survey Studies. Department of Mines and Technical Surveys, Ottawa. Water Survey Rep. No. 1.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.20 Inorganic Carbon: Carbonates and Bicarbonates

6.2.20.1 Introduction

Inorganic carbon compounds are composed primarily of carbonates, bicarbonates and carbonic acid. The presence of inorganic carbon influences the hardness of water, and can have detrimental effects on domestic and industrial uses of water. The use of hard water results in the formation of scale on boilers and pipes, and it can adversely affect textiles, plating and canning industries. Hard water use also results in increased soap consumption, which affects both domestic and industrial cleaning and laundering activities (McNeely *et al.* 1979).

Alkalinity is another parameter which is closely related to the amount of bicarbonate, carbonate and carbonic acid present in water (see Section 6.2.1). When waters with high alkalinity are boiled over an extended period of time, deposits may be formed, or the water may acquire an unpleasant taste. Waters with high alkalinity values can also affect the efficiency of wastewater treatment. Waters with low alkalinity are corrosive to pipes (see Section 6.2.11) (McNeely *et al.* 1979).

6.2.20.2 Sources and Pathways for Entering the Aquatic Environment

Inorganic carbon can enter the aquatic environment through dissolution of CO_2 in the atmosphere and biotic respiration. Carbon dioxide is readily soluble in water, but the amount of gas absorbed from any source depends on the partial pressure of carbon dioxide and the pH of the water. Water in contact with carbonate rock, such as limestone and dolomite, contributes bicarbonates and carbonates to the aquatic environment. Bicarbonate salts are used in industry because of their high solubility, and may be found in industrial waste effluent (McNeely *et al.* 1979).

In general, there are four sources of inorganic carbon in aquatic ecosystems: atmosphere, carbonate rocks, allochthonous inorganic carbon and biological cycling of autochthonous and allochthonous materials. The relative importance of these sources varies spatially and temporally. Carbon dioxide and/or bicarbonate (HCO_3^-) are incorporated into organic carbon by autotrophic organisms. The autochthonous organic carbon, plus any allochthonous organic material, are available as a pool of suspended organic carbon which tends to deposit in fresh water. Aerobic and anaerobic heterotrophic decomposition of both suspended and sedimented organic material results in the production of carbon dioxide, which is then available as a carbon source for autotrophs. Because the atmospheric and carbonate sources of inorganic carbon are considered to be constant in any given system, the rate of biological cycling of inorganic carbon represents the active part of that system (Allen and Kramer 1972).

6.2.20.3 Environmental Concentrations

The carbonate form of inorganic carbon is virtually absent in surface waters because their pH values do not often exceed 9; groundwaters, however, may be more alkaline, and may contain up to 10 mg·L^{-1} carbonate. A typical water with high sodium content may contain 50 mg·L^{-1} carbonate. The bicarbonate concentrations in surface waters are usually less than 500 mg·L^{-1}, and are frequently less than 25 mg·L^{-1}. The concentrations of total inorganic carbon in surface water are usually higher during low discharge periods because of greater groundwater influx (McNeely *et al.* 1979).

Environmental concentration ranges for bicarbonate and carbonate in Canadian surface waters are presented in Table 6-19 (NAQUADAT 1985).

6.2.20.4 Forms and Fate in the Aquatic Environment

In natural waters, the carbonate-bicarbonate system is part of the carbon cycle of the biosphere (see Section 6.2.20.2). In natural waters, the carbonate and bicarbonate ions and carbonic acid are maintained in equilibrium (Loewenthal and Marais 1976). The relative amounts of carbonates, bicarbonates and carbonic acid in water are related to the pH of the water, as shown in Figure 6-1 (Wetzel 1975). Their interaction in water results in a displacement of equilibrium between hydrogen and hydroxide ions. This displacement is manifested by the establishment of a specific pH (Loewenthal and Marais 1976). At pH 7-8, bicarbonate (HCO_3^-) predominates and constitutes 60-90% of total inorganic carbon.

6.2.20.5 References

Allen, H.E. and J.R. Kramer (eds.). 1972. Nutrients in Natural Waters. Environ. Sci. Technol. Ser. A. Wiley-Interscience Publ., New York. 457 pp.

Loewenthal, R.E. and G.V.R. Marais. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Application. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 433 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Total inorganic carbon. Carbonate-bicarbonate. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 10-12.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.21 Iron

6.2.21.1 Uses and Production

In Canada, iron ore is used in the manufacture of steel by integrated iron and steel producers in Hamilton and Sault Ste. Marie (Ontario), Contrecoeur (Quebec), and Sydney (Nova Scotia) (Catka 1983). Iron is also used in the production of paint pigments, plastics, polishing agents and electrical materials (Health and Welfare Canada 1980). Production, consumption, importation and exportation data on iron ore for 1983 and 1984 are presented in Table 6-20.

Table 6-19. Environmental Concentration Ranges for Bicarbonate and Carbonate in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Bicarbonate			
Western	1-877.7	2254	1980-1985
Carbonate			
Pacific	0	14	Prior to 1980
Western	0-74.5	2254	1980-1985
Central	0-24.2	1355	Prior to 1985

[1] Calculated values.

Source: NAQUADAT 1985.

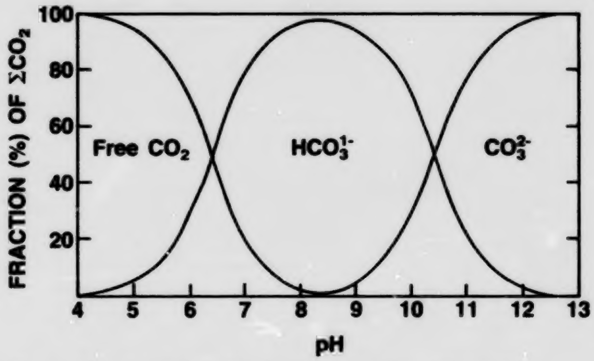


Figure 6-1. Speciation of inorganic carbon (from Wetzel 1975).

Table 6-20. Production, Consumption, Importation and Exportation of Iron Ore in Canada

	Amount (t)	
Parameter	1983	1984
Production (dry tonnes)	32 958 678	41 065 329
Consumption (of iron ore at Canadian iron and steel plants)	13 102 908	14 620 016
Importation (wet tonnes)	4 013 109	3 482 250
Exportation (all classes of iron ore in wet tonnes)	25 528 070	22 730 727

Source: Boyd 1985.

6.2.21.2 Sources and Pathways for Entering the Aquatic Environment

Iron is the fourth most abundant element in the earth's crust (Health and Welfare Canada 1980). The main iron deposits in Canada are located in Ontario, Quebec and Labrador (Boyd 1985). Iron minerals are widely distributed; the principal commercial iron ores are magnetite (Fe_3O_4), siderite ($FeCO_3$), limonite ($FeO(OH)$) and hematite (Fe_2O_3) (Health and Welfare Canada 1980).

Iron is naturally released into the environment from weathering of sulphide ores (pyrite, FeS_2) and igneous, sedimentary and metamorphic rocks. Leaching from sandstones releases iron oxides and iron hydroxides to the environment (McNeely *et al.* 1979).

Iron is also released into the environment by human activities, mainly from the burning of coke and coal, acid mine drainage (Bell 1975), mineral processing (McNeely *et al.* 1979), sewage (Oliver and Cosgrove 1975), landfill leachates (James 1977), iron-related industries (IJC 1976) and the corrosion of iron and steel (McNeely *et al.* 1979). Concentrations of iron in the Great Lakes range from 0.3 to 0.7 $mg\cdot L^{-1}$ near industrial sources (IJC 1976). A sample taken in 1982 from a British Columbia industrial wastewater station of NAQUADAT had a dissolved iron concentration of 0.33 $mg\cdot L^{-1}$ (detection limit 0.05 $mg\cdot L^{-1}$) (NAQUADAT 1985). Iron has been found in rainfall at concentrations of 0.05 $mg\cdot L^{-1}$ (McNeely *et al.* 1979).

6.2.21.3 Environmental Concentrations

Concentrations of iron in aerated surface waters are usually less than 0.5 $mg\cdot L^{-1}$. Environmental concentration ranges for iron in Canadian surface waters are presented in Table 6-21. In thermal hot springs and groundwaters, the concentration of iron may range from 10 to 100 $mg\cdot L^{-1}$ (McNeely *et al.* 1979). The average iron concentration for the Great Lakes is 0.12 $mg\cdot L^{-1}$ (IJC 1976). Iron levels in Canadian drinking water are usually less than 1 $mg\cdot L^{-1}$ (NAQUADAT 1976).

6.2.21.4 Forms and Fate in the Aquatic Environment

The two most common oxidation states of iron in water are the ferrous (Fe^{2+}) and the ferric (Fe^{3+}) states. In general, iron is present in surface waters in the ferric state. Ferric salts are insoluble in aerobic waters, and hence iron concentrations are usually low in the water column. In reducing waters, the ferrous form can persist and, in the absence of sulphide and carbonate anions, high concentrations of ferrous iron may be found. Iron may also occur as inorganic or organic ferrous and ferric complexes, or, in small quantities, as stable colloids or hydrosols (Hem 1972; McNeely *et al.* 1979; NAS 1979).

The chemical behaviour of iron in the aquatic environment is determined by oxidation-reduction reactions, pH and the presence of coexisting inorganic and organic complexing agents. Using chemical thermodynamic data, it has been predicted that ferrous iron will predominate at low pH in the absence of oxygen; some ferrous hydroxy complexes will be present at alkaline pH. At low pH (<3) in oxygenated water, the ferric ion predominates; however, at neutral and alkaline pH, hydroxide complexes are formed (Hem 1972; NAS 1979).

In the presence of oxygen, ferrous iron is oxidized and precipitates as ferric iron (McNeely *et al.* 1979). As a result, iron is usually found in the aquatic environment as colloidal suspensions of ferric hydroxide particles. These gels or flocs remain suspended in water or form flocculent materials that settle in the stream beds. With time, these flocs may harden and form a cement-like material that will consolidate bottom gravel (U.S. EPA 1976). Loose flocs of iron hydroxides can cause turbidity and decrease light penetration, thereby reducing primary productivity (IJC 1978). In anaerobic bottom waters and mud, ferrous iron, in the presence of hydrogen sulphide, will form ferrous sulphide, yielding black mineral muds (U.S. EPA 1976).

Table 6-21. Environmental Concentration Ranges for Iron in Canadian Surface Waters

Region	Concentration range ($mg\cdot L^{-1}$)	Number of samples	Sampling years
Pacific	ND[1,2]-54.0	147	1980-1985
	<0.03[3]-1.03	397	Prior to 1980
	0.039-11.0	97	1980-1985
Western	<0.02[3]-14.0	1926	1980-1985
	0.04[4]-11.0	627	1980-1985
Central	0.001[1]-7.55	1315	1980-1985
	0.002[3]-0.21	7	1985
	0.03[4]-2.97	158	1980-1985
Atlantic	0.004[1]-3.1	710	1980-1985
	0.0755[3]-0.17	8	1981
	0.01[4]-90.0	6449	1980-1985

[1] Detection limit is 0.001 $mg\cdot L^{-1}$ (total).
[2] ND = not detected.
[3] Detection limit is 0.001 $mg\cdot L^{-1}$ (dissolved).
[4] Detection limit is 0.05 $mg\cdot L^{-1}$ (extractable).

Source: NAQUADAT 1985.

Microorganisms and fungi in soil and subsurface environments may mobilize iron and bring it into solution. In anaerobic sediments, ferric oxide and hydroxides may be reduced when certain strains of microorganisms and an organic food source are present (Oborn and Hem 1961). Aerobic bacteria may catalyze the oxidation of ferrous iron, resulting in the precipitation of ferric hydroxide (Hem 1970). The growth cycles of freshwater algae and related aquatic microorganisms can influence the concentrations of iron in surface waters. The demand for iron during algal blooms can significantly reduce iron concentrations; iron taken up may then be released back into the water column upon death and decay of the plants (NAS 1979).

6.2.21.5 References

Bell, A.V. 1975. Base metal mine management in Canada. *In* Minerals and the Environment. Institute of Mining and Metallurgy, London. (Cited in Health and Welfare Canada 1980.)

Boyd, B.W. 1985. Iron ore. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 32-1 to 32-12.

Catka, C.J. 1983. Iron and steel. *In* Canadian Minerals Yearbook 1980. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 239-255.

Health and Welfare Canada. 1980. Iron. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 317-325.

Hem, J.D. 1970. Study and Interpretation of the Chemical Characteristics of Natural Water. 2nd edition. U.S. Geol. Surv. Water Supply Paper 1473. U.S. Government Printing Office, Washington, D.C. 363 pp. (Cited in NAS 1979.)

Hem, J.D. 1972. Chemical factors that influence the availability of iron and manganese in aqueous systems. Geol. Soc. Am. Spec. Pap. 140: 17-24. (Cited in Health and Welfare Canada 1980.)

IJC. 1976. Fourth Annual Report. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario. p. 45.

IJC. 1978. Iron. *In* Group 2 – New and Revised Specific Water Quality Objectives. Proposed for the 1972 Agreement Between the U.S. and Canada on Great Lakes Water Quality Criteria. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario. pp. 53-56.

James, S.C. 1977. Metals in municipal landfill leachate and their health effects. Am. J. Public Health 67: 429-432. (Cited in Health and Welfare Canada 1980.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Iron. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 20.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1979. Iron. National Academy of Sciences, U.S. National Research Council, University Park Press, Baltimore, Maryland. 248 pp.

Oborn, E.T. and J.D. Hem. 1961. Microbiologic factors in the solution and transport of iron. *In* Chemistry of Iron in Natural Water. U.S. Geol. Surv., Water Supply Paper 1459. U.S. Government Printing Office, Washington, D.C. pp. 213-235. (Cited in NAS 1979.)

Oliver, B.G. and E.G. Cosgrove. 1975. Metal concentrations in the sewage, effluents and sludges of some southern Ontario wastewater treatment plants. Environ. Lett. 9: 75-90. (Cited in Health and Welfare Canada 1980.)

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023.

6.2.22 Lead

6.2.22.1 Uses and Production

In Canada, the primary use of lead is in the production of acid-storage batteries. The second largest use is in the manufacture of chemical compounds, particularly alkyllead additives, such as tetramethyl- and tetraethyllead (Peeling 1975). Lead and its compounds are also used in electroplating, metallurgy, construction materials, coatings and dyes, electronic equipment, plastics, veterinary medicines, fuels and radiation shielding (Richard and Nriagu 1978; U.S. EPA 1980). Other uses of lead are for ammunition, corrosive-liquid containers, paints, glassware, fabricating storage tank linings, transporting radioactive materials, solder, piping, cable sheathing, roofing and sound attenuators (NRCC 1978; U.S. EPA 1980).

In 1984, Canadian mines produced 290 000 t of lead in concentrates, 40 000 t more than in 1983. Production of refined lead from primary lead plants totalled 173 000 t, 5000 t less than in 1983. Secondary lead production rose to 79 000 t from 58 000 t in 1983 (Bigauskas 1985). In 1982, production of refined lead from primary and secondary lead plants in Canada ranked third in the nonsocialist world for lead capacity and production behind the U.S.A. and Australia (Bigauskas 1985).

The principal Canadian ore producers are located in British Columbia (84 186 t), New Brunswick (73 250 t) and the Northwest Territories (88 355 t) (Bigauskas 1985); the only producers of refined lead are located in British Columbia and New Brunswick (Demayo *et al.* 1980).

Canadian consumption of lead used for batteries and battery oxides was 57 772 t in 1980, compared with 21 544 t for chemical uses such as white lead, red lead, litharge, tetramethyllead and tetraethyllead. Total consumption was 106 836 t in the same year (Bigauskas 1982).

6.2.22.2 Sources and Pathways for Entering the Aquatic Environment

Lead is a major constituent of more than 200 identified minerals, most of which are very rare. Several of these, however, are found in sufficient abundance to form mineral deposits. The most abundant is galena (PbS). The others are angelesite ($PbSO_4$), cerrusite ($PbCO_3$) (U.S. EPA 1979), crocoisite and morphite (Health and Welfare Canada 1980). The main sources of these minerals are igneous, metamorphic and sedimentary rocks (Health and Welfare Canada 1980; Crabtree 1985). Commercial ores have concentrations of lead in the range 30-80 $g{\cdot}kg^{-1}$ (Health and Welfare Canada 1980).

The principal natural pathway by which lead is released into the environment is weathering of sulphide ores, especially galena. It has been estimated that between 152 000 and 162 000 t of lead are mobilized globally by weathering each year (Demayo *et al.* 1980). Metallic lead and the common lead minerals are almost insoluble (Health and Welfare Canada 1980; U.S. EPA 1980). It has been estimated that approximately one-sixth of the weathered materials enters the environment in the dissolved form; the remainder enters associated with suspended sediments (Eriksson 1960).

Anthropogenic input of lead to the environment outweighs all natural sources. Lead reaches the aquatic environment through precipitation, fallout of lead dust, street runoff and industrial and municipal wastewater discharges (U.S. EPA 1976; Jaques 1985). In 1982, one sample taken from a British Columbia industrial wastewater station of NAQUADAT had a total lead concentration of 170 $\mu g{\cdot}L^{-1}$ (detection limit 50 $\mu g{\cdot}L^{-1}$) (NAQUADAT 1985). Mining, milling and smelting of lead and metals associated with lead, such as zinc, copper, silver, arsenic and antimony, as well as combustion of fossil fuels cause a loss of lead to aquatic ecosystems at a rate above that of normal weathering (U.S. EPA 1979; IJC 1980). For example, anthropogenic lead input to the oceans is about 10 times greater than that produced by natural weathering (McNeely *et al.* 1979). Total Canadian discharges of lead in effluents for 1982 were estimated at 562 t, with mining and milling accounting for 49 t (9%); smelting and refining, 29 t (5%); chemical manufacturing, 37 t (7%); pulp and paper mills, 9 t (2%); municipal sewage, 412 t (73%); and other sources, 27 t (5%) (Jaques 1985).

Total anthropogenic emissions of lead for 1982 were estimated at 11 466 t. Gasoline-powered motor vehicles accounted for an estimated 7000 t, or 61% of the total. Emissions from copper and nickel smelters were estimated at 1706 t for 1982, or 15% of the total. Mining, milling and concentrating of lead-bearing ores accounted for 964 t, or 8%, and primary iron and steel production contributed 600 t, or 5% of the total emissions for 1982. The remaining 4% of emissions was contributed by other miscellaneous sources. There has been an overall decline in lead emissions of 21% since 1978, primarily because of a reduction in the use of leaded gasoline and improved emission controls in industry (Jaques 1985). Lead loading from precipitation in the Great Lakes Basin ranges from 9 to 20 $mg{\cdot}m^{-2}$ per year, but loadings in excess of 6000 $mg{\cdot}m^{-2}$ per year have been recorded in highly contaminated areas in Canada (IJC 1980).

6.2.22.3 Environmental Concentrations

Lead ranks as the 36th element in order of abundance based on its concentration in the earth's crust (igneous rocks), estimated at 12.5 mg·kg^{-1} (Taylor 1964). Other estimates place the average concentration of lead at 15-16 mg·kg^{-1} (de Treville 1964; Lovering 1976). Sedimentary rocks have been estimated to contain 7 mg·kg^{-1} (sandstone), 20 mg·kg^{-1} (shale) and 9 mg·kg^{-1} (limestone) of lead (Turekian and Wedepohl 1961).

The levels of dissolved lead in natural surface waters are generally low. The sulphides, sulphates, oxides, carbonates and hydroxides of lead are almost insoluble, whereas the carbonates and hydroxides are considered to impose an upper limit on the concentration of lead that might occur in lakes, rivers and groundwaters (Hem and Durum 1973). It has been estimated that the global mean lead concentration in lakes and rivers is between 1.0 and 10.0 μg·L^{-1} (Livingstone 1963). Open lake concentrations up to 100 μg·L^{-1} have been reported for the Great Lakes; however, recent data suggest that the levels in open lake waters are closer to 1.0 μg·L^{-1} (IJC 1980).

River and lake water samples collected between 1972 and 1977 in Canada ranged from <1.0 to ~50.0 μg·L^{-1} for dissolved lead and <1.0 to 100 μg·L^{-1} for extractable lead (NAQUADAT 1978). An intensive water quality survey of the Niagara River found concentrations ranging from nondetectable to 1.0 μg·L^{-1} for dissolved lead and nondetectable to 7.0 μg·L^{-1} for total lead (Chan 1977). Lead concentrations in the Great Lakes ranged from 1 to 12 μg·L^{-1} (Weiler and Chawla 1969). Lakes sampled in the Sudbury Region had a concentration range for lead of 27-103 μg·L^{-1} (Stokes *et al.* 1973).

Lead has been accumulating in Great Lakes sediments at a rate above that from normal weathering and erosion since the arrival of the early settlers (Nriagu *et al.* 1979). The mean depositional zone (deep, relatively slow water movement) lead concentrations for the Great Lakes ranged from 60 to 154 mg·kg^{-1} (dry weight) (IJC 1977a). The Ottawa River was found to have a sediment concentration range of 9-314 mg·kg^{-1} (dry weight) (Oliver and Agemian 1974). A Burnaby, B.C., mountain stream (open space and residential) had a concentration range of 4-63.2 mg·kg^{-1} of lead in sediment (Hall and Fletcher 1974).

Environmental concentration ranges for lead in Canadian surface waters are presented in Table 6-22.

The lead concentration in Canadian tap water is generally low, with an average concentration of 7.6 μg·L^{-1}. Ninety-eight percent of 266 NAQUADAT stations sampling household tap water reported lead concentrations of 50 μg·L^{-1} or less (NAQUADAT 1976). Lead concentrations as high as 2600 μg·L^{-1} were recorded in tap water after overnight nonuse in lead plumbing (Wong and Berrang 1976).

6.2.22.4 Forms and Fate in the Aquatic Environment

Lead exists in several oxidation states, 0, +1, +2 and +4, all of which, with the possible exception of Pb(I), are of environmental importance (U.S. EPA 1979; Demayo *et al.* 1980). The divalent form, Pb(II), is the stable ionic species in most of the natural environment (U.S. EPA 1979). In the aquatic environment, lead may be complexed with organic ligands, yielding soluble, colloidal and particulate compounds. The exact nature of these ligands is not known, although it is known that lead can be sorbed by humic acids (Corrin and Natusch 1977).

Table 6-22. Environmental Concentration Ranges for Lead in Canadian Surface Waters

Region	Concentration range[1] (μg·L^{-1})	Number of samples	Sampling year(s)
Pacific	1-4	12	1980-1984
Western	1-77[2]	1848	1980-1983
Central	1-46	1495	1980-1984
Atlantic	1-41	229	1980-1983

[1] Detection limit is 1 μg·L^{-1} (total).
[2] Detection limit is 4 μg·L^{-1} (total recoverable).

Source: NAQUADAT 1985.

Chemical speciation of lead compounds in water is complex, and depends upon several modifying factors including pH, dissolved oxygen and the presence of coexisting inorganic and organic compounds. Much of the information on lead speciation comes from model studies. Solubility of lead compounds is the primary control mechanism; the sulphides, sulphates, oxides, carbonates and hydroxides of lead are insoluble (Hem and Durum 1973).

Soluble lead, whether natural, from industrial sources or from photolysis (U.S. EPA 1979) of atmospheric lead compounds (e.g. lead halides), is removed from solution by association with sediments and suspended particulates, such as organic matter, hydrous oxides and clays (Leland *et al.* 1974). Solubility calculations show that lead solubility is very low (<1 μg·L^{-1} at pH 8.5-11) in water containing lead, carbon dioxide and sulphur and in strongly reducing environments of low pH (pH ~2). Between pH 6 and 8, solubility of lead is a complex function of pH and dissolved CO_2. At constant pH, the solubility of lead decreases with increasing alkalinity. Below pH 6.5, the solubility of lead increases. For example, the solubility of lead can be as high as 0.33 mg·L^{-1} at pH 6.5 and an alkalinity of approximately 25 mg·L^{-1} (Hem 1976). At the low lead concentrations typically found in the aquatic environment, most of the lead in the dissolved phase may be complexed by organic ligands (Ramamoorthy and Kushner 1975).

Sorption is the dominant mechanism controlling the distribution of lead in the aquatic environment. In the presence of clay suspensions at pH 5-7, most of the lead is precipitated and sorbed, probably as sparingly soluble hydroxides. Below about pH 5-6, the formation of stable cationic species can prevent the formation of hydroxides (Farrah and Pickering 1977).

There is no evidence to indicate that photolysis of lead compounds plays a significant role in the removal of lead from the water column; it is, however, an important process in the atmosphere. The ultimate products of photodegradation of atmospheric organolead compounds are lead oxides and halides, which will enter the aquatic environment via direct deposition or surface runoff (Hirschler and Gilbert 1964).

Tetramethyllead, which can be biologically and chemically produced in anaerobic sediments, is volatile (Wong *et al.* 1975). However, in aerobic waters overlying reducing sediments, it is expected that any tetramethyllead released from the sediments would not be stable. Hence, volatilization is not considered to be a significant removal process (U.S. EPA 1979).

Lead is bioaccumulated by aquatic organisms, including benthic bacteria (Patrick and Loutit 1976), freshwater plants, invertebrates and fish (Chapman *et al*. 1968). Wet weight bioconcentration factors for these organisms range from 20 to 360 (Chapman *et al*. 1968; Patrick and Loutit 1976; Keeney *et al*. 1976). A concentration factor above 10^6 was reported for phytoplankton from the English Lake District (Denny and Welsh 1979). Pumpkinseed sunfish (*Lepomis gibbosus*) accumulated lead mainly in the gill, liver and fin tissues, and less in the muscle tissue. This study also showed that fish held at pH 6.0 accumulated three times as much lead as fish held at pH 7.5 (Merlini and Pozzi 1977). Decreasing pH increases the availability of divalent lead, the principal form believed to be accumulated by aquatic biota (U.S. EPA 1979). In areas of local contamination in the Great Lakes, e.g. Toronto Harbour, lead concentrations in fish tissue were 1.78 $\mu g \cdot g^{-1}$ (Brown and Chow 1975). Elsewhere in the Great Lakes, muscle lead concentrations were uniform at less than 0.5 $\mu g \cdot g^{-1}$ (Uthe and Bligh 1971; IJC 1977b). The exception was found at the St. Lawrence River near Maitland, where organic lead discharges from a tetramethyllead production plant resulted in elevated levels of lead in several sport and commercial fish species. That plant is now closed, and it is expected that lead levels in fish tissues will quickly decline (Crabtree 1985). Microcosm studies indicate that lead is not biomagnified (Lu *et al*. 1985).

6.2.22.5 References

Bigauskas, J. 1984. Lead. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report No. 32.

Bigauskas, J. 1985. Lead. Can. Min. J. 106(2): 54.

Brown, J.R. and L.Y. Chow. 1975. The comparison of heavy metals in fish samples taken from Baie du Dore, Lake Huron and Toronto Harbour, Lake Ontario. Int. Conf. on Heavy Metals in the Environment, Toronto, Ontario.

Chan, C.H. 1977. Water Quality Surveys on the Niagara River – 1974. Water Quality Branch, Ontario Region, Fisheries and Environment Canada, Burlington, Ontario. Rep. Ser. No. 48.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Corrin, M.L. and D.F.S. Natusch. 1977. Physical and chemical characteristics of environmental lead. *In* Lead in the Environment. W.R. Boggess and B.G. Wixson (eds.). Prepared for the National Science Foundation. NSF/RA-770214. pp. 7-31.

Crabtree, P. 1985. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Demayo, A., M.C. Taylor and S.W. Reeder. 1980. Lead. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Denny, P. and R.P. Welsh. 1979. Lead accumulation in plankton blooms from Ullswater, the English Lake District. Environ. Pollut. 18: 335-346.

de Treville, R.T.P. 1964. Natural occurrence of lead. Arch. Environ. Health 8: 212-221. (Cited in Health and Welfare Canada 1980.)

Eriksson, E. 1960. The yearly circulation of chloride and sulfur in nature: meteorological, geochemical and pedological implications. Part II. Tellus 12: 63-109. (Cited in Demayo *et al*. 1980.)

Farrah, H. and W.F. Pickering. 1977. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water Air Soil Pollut. 8: 189-197.

Hall, K.J. and K. Fletcher. 1974. Trace metal pollution from a metropolitan area: sources and accumulation in the lower Fraser River and estuary. *In* Proc. Int. Conf. on Transport of Persistent Chemicals in Aquatic Ecosystems, May 1-3, Ottawa. pp. I-83 to I-87.

Health and Welfare Canada. 1980. Lead. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 327-348.

Hem, J.D. 1976. Inorganic chemistry of lead in water. *In* Lead in the Environment. T.G. Lovering (ed.). U.S. Geol. Surv. Prof. Pap. 957. Washington, D.C. pp. 5-11. (Cited in Demayo *et al*. 1980.)

Hem, J.D. and W.H. Durum. 1973. Solubility and occurrence of lead in surface water. J. Am. Water Works Assoc. 65: 562-568.

Hirschler, A. and L.F. Gilbert. 1964. Nature of lead in automobile exhaust gas. Arch. Environ. Health 8: 297-313.

IJC. 1977a. Annual Progress Report of the International Reference Group on Great Lakes Pollution from Land Use Activities. International Joint Commission, Windsor, Ontario.

IJC. 1977b. The Water of Lake Huron and Lake Superior. Vol. III. Parts A and B. Upper Lakes Reference Group Report. International Joint Commission, Windsor, Ontario.

IJC. 1980. Lead. *In* Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario. pp. 63-113.

Jaques, A.P. 1985. National Inventory of Sources and Releases of Lead (1982). Environmental Protection Service, Environment Canada, Ottawa. 39 pp.

Keeney, W.L., W.G. Breck, G.W. Van Loon and J.A. Pag. 1976. The determination of trace metals in *Cladophora glomerata* as a potential biological monitor. Water Res. 10: 981-984.

Leland, H.V., S.S. Shukla and N.F. Shimp. 1974. Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan. *In* Trace Metals and Metal-Organic Interactions in Natural Waters. P.C. Singer (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. (Cited in Health and Welfare Canada 1980.)

Livingstone, D.A. 1963. Data of Geochemistry. 6th edition. Chapter of Chemical Composition of Rivers and Lakes. U.S. Geol. Surv. Prof. Pap. 440. (Cited in WHO 1977.)

Lovering, T.G. (ed.). 1976. Lead in the Environment. U.S. Geol. Surv. Prof. Pap. 957. Washington, D.C.

Lu, P.-Y., R.L. Metcalf, R. Furman, R. Vogel and J. Hassett. 1975. Model ecosystem studies of lead and cadmium and of urban sewage sludge containing these elements. J. Environ. Qual. 4: 505-509.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Lead. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 20-21.

Merlini, M. and A. Pozzi. 1977. Lead and freshwater fishes. Part 1. Lead accumulation and water pH. Environ. Pollut. 12: 168-172.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1978. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1978. Effects of Lead in the Environment – Quantitative Aspects. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16736. 779 pp.

Nriagu, J.O., A.L.W. Kemp, H.K.T. Wong and N. Harper. 1979. Sedimentary record of heavy metal pollution in Lake Erie. Geochim. Cosmochim. Acta 43: 247-258.

Oliver, B.G. and H. Agemian. 1974. Further Studies on the Heavy Metal Levels in Ottawa and Rideau River Sediments. Inland Waters Directorate, Environment Canada, Ottawa. Sci. Ser. 37. pp. 1-10.

Patrick, F.M. and M. Loutit. 1976. Passage of metals in effluents, through bacteria to higher organisms. Water Res. 10: 333-335.

Peeling, G.R. 1975. Lead. *In* Canadian Minerals Yearbook 1974. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

Ramamoorthy, S. and D.J. Kushner. 1975. Heavy metal binding components of river water. J. Fish. Res. Board Can. 32: 1755-1766.

Richard, D.T. and J.O. Nriagu. 1978. Aqueous environmental chemistry of lead. *In* The Biogeochemistry of Lead in the Environment. Part A. J.O. Nriagu (ed.). Elsevier/North-Holland, New York.

Stokes, P.M., T.C. Hutchinson and K. Krauter. 1973. Heavy metal tolerance in algae isolated from polluted lakes near the Sudbury, Ontario smelters. Water Pollut. Res. Can. 8: 178-201.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285.

Turekian, K.K. and K.H. Wedepohl. 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72: 175-192. (Cited in Demayo *et al.* 1980.)

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 82-94.

U.S. EPA. 1979. Lead. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 13-1 to 13-19.

U.S. EPA. 1980. Ambient Water Quality Criteria for Lead. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-057.

Uthe, J.F. and E.G. Bligh. 1971. Preliminary survey of heavy metal contamination of Canadian freshwater fish. J. Fish. Res. Board Can. 28: 786-788.

Weiler, R.R. and V.R. Chawla. 1969. Dissolved mineral quality of Great Lakes waters. *In* Proc. 12th Conf. on Great Lakes Res., May 5-7, Ann Arbor, Michigan. pp. 801-818.

WHO. 1977. Environmental Health Criteria. Vol. 3. Lead. World Health Organization, Geneva. p. 31.

Wong, C.S. and P. Berrang. 1976. Contamination of tap water by lead pipe and solder. Bull. Environ. Contam. Toxicol. 15: 530-534.

Wong, P.T.S., Y.K. Chau and P.L. Luxon. 1975. Methylation of lead in the environment. Nature (London) 253: 263-264.

6.2.23 Lithium

6.2.23.1 Uses and Production

Lithium is used in metallurgy, in the manufacture of glass and ceramics, lubricants and storage batteries and in dehumidifying processes. It is also used medicinally for the treatment of manic-depressive disorders. Lithium may also be found in the ash from coal combustion (McNeely *et al.* 1979).

No production of lithium occurs in Canada at present. The only lithium-producing mine in Canada, located near Val D'Or, Quebec, closed in 1965 (Stonehouse 1985). Until January 1, 1983, when operations were suspended, the Tantalum Mining Corp. (Canada) Ltd., at Bernie Lake in southeastern Manitoba, had mined the Tanco pegmatite deposit for its tantalum-bearing minerals and the mineral spodumene (containing lithium). Production data are unavailable for reasons of confidentiality; however, preproduction reserves for lithium in spodumene were estimated at 6 624 133 t at a grade of 2.76% Li_2O (Crouse *et al.* 1984). The U.S.A., U.S.S.R., China and Zimbabwe are the four significant world producers of prime lithium concentrate. Total global lithium-mineral production for 1978 (the most recent data available) can be only partially estimated, because the U.S.A. has withheld its production figures to avoid disclosing company proprietary data. The partial world estimate is as follows: South America, 102.5 t; Africa, 235.9 t; U.S.S.R., 1179.4 t; and China, 272.2 t (U.S. Department of the Interior 1980). In 1981 and 1982, 32 t and 21 t, respectively, of lithium salts of inorganic acids were imported into Canada (Statistics Canada 1983). Spodumene is also imported into Canada, but no figures are available (Statistics Canada 1983). Importation data are not available for lithium.

Table 6-23. Environmental Concentration Ranges for Lithium in Canadian Surface Waters

Region	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<5[1]-69	3	Prior to 1980
	<5[2]-25	20	Prior to 1980
Western	<5[1]-9	11	1980
	<5[2]-190	79	Prior to 1980
Central	<5[1]	50	Prior to 1980
	1[2]-7	249	Prior to 1980
Atlantic	<2[1]-10	56	Prior to 1980

[1] Detection limit is 5 $\mu g \cdot L^{-1}$ (extractable).

[2] Detection limit is 5 $\mu g \cdot L^{-1}$ (dissolved).

Source: NAQUADAT 1985.

6.2.23.2 Sources and Pathways for Entering the Aquatic Environment

Aluminosilicates and phosphates, such as spodumene ($LiAlSi_2O_6$), petalite ($LiAlSi_4O_{10}$) and amblygonite [$(Li,Na)Al(PO_4)(F,OH)$], are the main mineral sources of lithium. Lithium is easily leached from these materials, but input to the aquatic environment is small. The average lithium concentrations in igneous rocks, sandstone, shale and carbonates are 32, 15, 46 and 5.2 $\mu g \cdot g^{-1}$, respectively (Faust and Aly 1981).

The industrial uses outlined in Section 6.2.23.1 may be significant anthropogenic sources of lithium to surface waters (McNeely *et al.* 1979).

6.2.23.3 Environmental Concentrations

Most surface waters contain lithium at concentrations below 10 $mg \cdot L^{-1}$. Waters containing chloride and sulphate have higher lithium concentrations than do waters containing bicarbonate. Environmental concentration ranges for lithium in Canadian surface waters are presented in Table 6-23. Lithium concentrations have been recorded as extractable and dissolved in NAQUADAT (1985). Brines and hot springs may also contain lithium in excess of 10 $mg \cdot L^{-1}$. Seawater lithium concentrations are approximately 0.17 $mg \cdot L^{-1}$ (McNeely *et al.* 1979).

6.2.23.4 Forms and Fate in the Aquatic Environment

Lithium, one of the alkali metals, occurs in the +1 oxidation state in nature. Lithium compounds are extremely soluble and tend to remain in solution (Windholtz *et al.* 1983). Lithium is easily leached from rocks and sediments and usually occurs with sodium in aqueous solutions (McNeely *et al.* 1979).

6.2.23.5 References

Crouse, R.A., P. Cerny, D.L. Trueman and R.O. Burt. 1984. The Tanco pegmatite, southeastern Manitoba. *In* The Geology of Industrial Minerals in Canada. Spec. Vol. 29. G.R. Guillet and W. Martin (eds.). The Canadian Institute of Mining and Metallurgy, Montreal.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Lithium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 21-22.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Stonehouse, D. 1985. Personal communication. Mineral Policy Sector, Energy, Mines and Resources Canada, Ottawa.

U.S. Department of the Interior. 1980. Lithium. *In* Mineral Facts and Problems. Bureau of Mines, Washington, D.C. pp. 521-525.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. Merck & Co., Inc., Rahway, New Jersey.

6.2.24 Magnesium

6.2.24.1 Uses and Production

Magnesium is used in the textile, tanning and paper industries. Alloys of magnesium are used extensively in molds, die castings, extrusions, rolled sheets and plate forgings, mechanical handling equipment, portable tools, luggage and general household goods. The carbonates, chlorides, hydroxides, oxides and sulphates of magnesium are used in the production of magnesium metal, refractories, fertilizers, ceramics, explosives and medicinals (Beck 1966; Bokovay 1985).

Production, consumption, importation and exportation of magnesium in Canada are presented in Table 6-24. World production for magnesium in 1981, 1982 and 1983 was 208 500, 156 400 and 156 000 t, respectively (Bokovay 1985).

Table 6-24. Production, Consumption, Importation and Exportation of Magnesium in Canada

	Amount (t)		
Parameter	1981	1982	1983
Production	8800	7900	7800
Consumption	6387	5005	NA[1]
Importation	3249	1972	3714
Exportation	6221	4501	2500

[1] NA = not available; consumption has increased significantly in 1983 and also in 1984.

Source: Bokovay 1985.

6.2.24.2 Sources and Pathways for Entering the Aquatic Environment

Magnesium is the eighth most abundant natural element (Durfor and Becker 1972). Natural sources contribute more magnesium to the environment than do all anthropogenic sources. Magnesium is commonly found in magnesite, dolomite, olivine, serpentine, talc and asbestos minerals. The principal sources of magnesium in natural water are ferromagnesium minerals in igneous rocks and magnesium carbonates in sedimentary rocks.

Annual loadings of magnesium are available for Lake Superior and Lake Huron. Direct industrial and municipal effluents during the period between 1973 and 1975 contributed 9.2 and 3.6 $t \cdot a^{-1}$, respectively, but the major inputs were from tributaries flowing into the lakes: 990 and 1250 t of magnesium flowed annually into Lake Superior and Lake Huron, respectively. Atmospheric deposition was also greater than direct industrial input, with 15.3 and 22.5 t, respectively, being deposited annually onto the lakes (IJC 1976).

Table 6-25. Environmental Concentration Ranges for Magnesium in Canadian Surface Waters

Region	Concentration range ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	14.0[1]-18.0	33	1980
Western	44[2]-181	4	Prior to 1980
	0.03[1]-168	2 932	1980-1985
Central	ND[2,3]-1000	2 700	Prior to 1980
	0[1]-24.2	4 461	1980-1985
Atlantic	ND[2]-954.0	17 217	Prior to 1980
	0.1[4]-37	6 661	1980-1985
	0.1[1]-680.0	2 345	1980-1985

[1] Detection limit is 0.1 $mg \cdot L^{-1}$ (dissolved).
[2] Detection limit is 0.05 $mg \cdot L^{-1}$ (total).
[3] ND = not detected.
[4] Detection limit is 0.005 $mg \cdot L^{-1}$ (dissolved).

Source: NAQUADAT 1985.

6.2.24.3 Environmental Concentrations

Water in watersheds with magnesium-containing rocks may contain magnesium in the concentration range of 1-100 $mg \cdot L^{-1}$. The sulphates and chlorides of magnesium are very soluble, and water in contact with such deposits may contain several hundred milligrams of magnesium per litre (Durfor and Becker 1972).

Environmental concentration ranges for magnesium in Canadian surface waters are presented in Table 6-25.

6.2.24.4 Forms and Fate in the Aquatic Environment

Magnesium is abundant in the earth's crust and is a common constituent of natural water. Along with calcium, it is one of the main contributors to water hardness (see Section 6.2.19). Like other alkaline earth metals, magnesium exists primarily in the +2 oxidation state. Univalent magnesium compounds exist usually only under very exceptional circumstances. Numerous organometallic compounds involving magnesium exist (Cotton and Wilkinson 1980).

The aqueous chemistry of magnesium is similar to that of calcium, such that carbonates and oxides are formed. Magnesium compounds are, in general, more soluble than their calcium counterparts. As a result, large amounts of magnesium are rarely precipitated. Magnesium carbonates and hydroxides precipitate at high pH (>10). Magnesium concentrations can be extremely high in certain closed saline lakes (Wetzel 1975).

Magnesium is considered to be an essential element for all organisms. It may be accumulated in calcareous tissues, and has been found in edible vegetables (700-5600 mg·kg^{-1}), marine algae (6400-20 000 mg·kg^{-1}), marine fish (1200 mg·kg^{-1}) and mammalian muscle (900 mg·kg^{-1}) and bone (700-1800 mg·kg^{-1}) (Bowen 1979). Magnesium is one of the principal cations of soft tissue (Health and Welfare Canada 1975).

6.2.24.5 References

Beck, A.V. (ed.). 1966. The Technology of Magnesium and Its Alloys. *In* McGraw-Hill Encyclopedia of Science and Technology. 3rd edition. McGraw-Hill, Toronto, Ontario.

Bokovay, G. 1985. Magnesium. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 37.1-37.7.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Durfor, C.J. and E. Becker. 1972. Constituents and properties of water. *In* Water Quality in a Stressed Environment. W.A. Pettyjohn (ed.). Burgess Publ. Co., Minneapolis, Minnesota. pp. 24-41. (Cited in Health and Welfare Canada 1980.)

Health and Welfare Canada. 1975. Dietary Standard for Canada. Health Protection Branch, Ottawa.

Health and Welfare Canada. 1980. Magnesium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 359-369.

IJC. 1976. The Waters of Lake Huron and Lake Superior. Vol. 1. Summary and Recommendations. Report by the Upper Lakes Reference Group, International Joint Commission, Windsor, Ontario. pp. 45-59.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.25 Manganese

6.2.25.1 Uses and Production

Manganese, its alloys and manganese compounds are commonly used in the steel industry in the manufacturing of metal alloys and dry cell batteries, and in the chemical industry in paints, varnishes, inks, dyes, glass, ceramics, matches, fireworks and fertilizers (McNeely *et al.* 1979).

No manganese production is carried out in Canada. In 1982, iron and steel industries imported 25 088 t of ferromanganese, 2877 t of silicomanganese, 71 655 t of manganese ore and 781 t of manganese metal into Canada. Canadian consumption in 1982 was 130 826 t of manganese ore and 69 166 t of ferromanganese and silicomanganese combined. World production of manganese ores was 23 081 000 t in 1982 (Phillips 1985).

6.2.25.2 Sources and Pathways for Entering the Aquatic Environment

Soils, sediments and metamorphic and sedimentary rocks are significant natural sources of manganese. Manganese is widely distributed, contributing about 0.085% of the earth's crust. It occurs in a number of ores, the most important being pyrolusite (MnO_2). Other manganese ores are mainly oxides, hydrous oxides and the carbonate, $MnCO_3$ (NAS 1973). Ferromanganese minerals, such as biotite mica ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$) and amphibole ($((Mg,Fe)_7$-$Si_8O_{22}(OH)_2)$), contain large amounts of manganese. The weathering of surficial manganese deposits contributes small amounts of manganese to natural waters (NAS 1973; McNeely *et al.* 1979).

Industrial discharges can account for elevated concentrations of manganese in receiving water. Industrial wastewater sampled from a NAQUADAT station in British Columbia had maximum manganese concentrations of 24 mg·L^{-1} (total), 6.4 mg·L^{-1} (dissolved) and 31 mg·L^{-1} (extractable) during the period between 1981 and 1983 (NAQUADAT 1985). The iron and steel industry and acid mine drainage, in particular, release a large portion of the manganese found in the environment. Iron and steel plants also release manganese into the atmosphere, where it is then redistributed through atmospheric deposition (McNeely *et al.* 1979).

The most recent emissions data on manganese in the Canadian environment were reported in 1972. Total emissions of manganese to the atmosphere in 1972 were estimated at 6010 t. The ferromanganese and silicomanganese industry accounted for 62%, or 3695 t, of the total. Emissions from the primary iron and steel industry accounted for 37%, or 2199 t. Ontario accounts for 65% of total Canadian manganese emissions, followed by Quebec with 23% (Environment Canada 1976).

6.2.25.3 Environmental Concentrations

Manganese seldom reaches concentrations of 1.0 mg·L^{-1} in natural surface waters, and is usually present in quantities of 0.2 mg·L^{-1} or less. Environmental concentration ranges for manganese in Canadian surface waters are presented in Table 6-26. Concentrations higher than 0.2 mg·L^{-1} may occur in groundwaters and deep stratified lakes and reservoirs under reducing conditions. A groundwater well in Newfoundland was reported to have a concentration range of 7.9-9.5 mg·L^{-1} for extractable manganese, based on two samples taken in 1981 (NAQUADAT 1985). Subsurface and acid mine waters may contain 10 mg·L^{-1}, and some reservoirs may have concentrations of 150 mg·L^{-1} (McNeely *et al.* 1979). In Nova Scotia, concentrations as high as 4.6 mg·L^{-1} were reported for one drinking water supply (Health and Welfare Canada 1980).

6.2.25.4 Forms and Fate in the Aquatic Environment

Manganese may exist in oxidation states ranging from −3 to +7; the divalent and tetravalent states are of primary importance in aqueous systems. Manganese is similar to iron in its chemical behaviour, and is frequently found in association with iron. It may exist in the manganous (Mn^{2+}) form, but it is readily oxidized to the manganic (Mn^{4+}) form (McNeely *et al.* 1979). In the absence of dissolved oxygen, however, the divalent state predominates (U.S. EPA 1973). Permanganates (Mn^{7+}) are not persistent because they rapidly oxidize organic

Table 6-26. Environmental Concentration Ranges for Manganese in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.01-1.70	155	1980-1985
	0.01[2]	2	1982
	0.01-0.43[3]	183	1980-1985
Western	0.01-4.0[2]	2129	1980-1985
	0.01-4.8[3]	648	1980-1985
Central	0.001-0.26	1292	1980-1985
	0.01-0.06[2]	145	1980-1985
	0.01-0.4[3]	235	1980-1985
Atlantic	0.002-0.737	464	1980-1985
	0.01-0.24[2]	8	1980-1981
	0.01-3.80[3]	7504	1980-1985

[1] Detection limit is 0.001 mg·L^{-1}.

[2] Dissolved manganese.

[3] Extractable manganese.

Source: NAQUADAT 1985.

materials and are thereby reduced (McKee and Wolf 1963). Nitrate, sulphate and chloride salts of manganese are quite soluble in water, whereas oxides, carbonates, phosphates, sulphides and hydroxides are only sparingly soluble (Cotton and Wilkinson 1980).

Pronounced changes in dissolved manganese concentrations may be caused by changes in redox potential, dissolved oxygen, pH and organic matter (Delfino and Lee 1968; Slack and Feltz 1968; Spencer and Brewer 1971; Howard and Chisholm 1975; Wetzel 1975). In natural waters, a substantial fraction of manganese is present in suspended form. In surface waters, divalent manganese will be rapidly oxidized to manganese dioxide, which will then undergo sedimentation. In the presence of complex-forming inorganic and organic compounds, the colloidal stability of manganese oxides will be enhanced. Alternatively, in areas of low dissolved oxygen or in anaerobic areas at low pH, soluble manganese forms may persist (Stumm and Morgan 1970). The presence of organic matter in water stabilizes manganese solutions, perhaps as a result of the formation of complex ions by organic compounds (NAS 1973).

Manganese is an essential trace element for microorganisms, plants and animals, and, hence, is contained in all or nearly all organisms. Marine organisms are capable of concentrating manganese to many times the concentrations found in seawater. For example, manganese enrichment factors for shellfish range from 10^3 to 10^4, whereas enrichment factors for marine algae, plants and fish were found to be 10^4, 10^5 and 10^2, respectively (NAS 1973). Manganese was found to have a biological half-life of approximately 46 d in bluegill sunfish (*Lepomis macrochirus*) (Miller *et al.* 1980).

6.2.25.5 References

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Delfino, J.J. and G.F. Lee. 1968. Chemistry of manganese in Lake Mendota, Wisconsin. Environ. Sci. Technol. 2: 1094-1100.

Environment Canada. 1976. National Inventory of Sources and Emissions of Manganese (1972). Air Pollution Control Directorate, Environmental Protection Service, Ottawa. Intern. Rep. APCD 75-6.

Health and Welfare Canada. 1980. Manganese. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 371-385.

Howard, H.H. and S.W. Chisholm. 1975. Seasonal variation of manganese in a eutrophic lake. Am. Midl. Nat. 93: 188-197. (Cited in Thurston *et al.* 1979.)

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. Publ. No. 3-A. State Water Quality Control Board, Sacramento, California. 548 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Manganese. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 22-23.

Miller, D.W., R.J. Vetter and G.J. Atchinson. 1980. Effect of temperature and dissolved oxygen on uptake and retention of ^{54}Mn in fish. Health Phys. 33: 221-225.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1973. Manganese. Medical and Biologic Effects of Environmental Pollutants. Division of Medical Sciences, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 191 pp.

Phillips, D.R. 1985. Manganese. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 38.1-38.7.

Slack, K.V. and H.R. Feltz. 1968. Tree leaf control on low-flow water quality in a small Virginia stream. Environ. Sci. Technol. 2: 126-131.

Spencer, D.W. and P.G. Brewer. 1971. Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. J. Geophys. Res. 76: 5877-5892.

Stumm, W. and J.J. Morgan. 1970. Aquatic Chemistry. Wiley-Interscience, New York. 583 pp.

Thurston, R.V., R.C. Russo, C.M. Fetterolf, T.A. Edsall and Y.M. Barber (eds.). 1979. A Review of the EPA Red Book: Quality Criteria for Water. Water Quality Section, American Fisheries Society, Bethesda, Maryland.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.26 Mercury

6.2.26.1 Uses and Production

Mercury is used in the chlor-alkali industry, which produces chlorine, caustic soda (sodium hydroxide) and hydrogen, and the paint industry in paint pigments and preservatives (Hocking 1979; Health and Welfare Canada 1980). Other uses of mercury include pulp and paper manufacture; thermometers; electrical equipment, such as mercury switches, batteries and fluorescent and mercury vapour lamps; dental amalgams; and some therapeutic medicinal compounds. Mercury-based pesticides were once used in agriculture; the use of such pesticides has, however, been restricted (McNeely *et al.* 1979; Reeder *et al.* 1979; Health and Welfare Canada 1980; U.S. EPA 1980).

Table 6-27. Importation of Mercury and Some Mercury Compounds into Canada

Compound	Amount (t) 1981	Amount (t) 1982
Mercury (metal)	48	52
Mercury oxide	50	15
Mercurous chloride	194	2
Mercuric chloride	11	2
Mercuric sulphide	0.05	0.2

Source: Statistics Canada 1983.

There has been no mining of mercury in Canada since 1975. World production of mercury in 1980 was estimated at 6557 t. In the same year, Canada imported 50 t of elemental mercury, of which 36.3 t were consumed. The decline of mercury consumption in Canada from a peak of 154 t in 1970 is partly because of environmental concerns (Hogan 1983). Various mercury compounds imported into Canada are presented in Table 6-27.

6.2.26.2 Sources and Pathways for Entering the Aquatic Environment

Mercury deposits occur in all types of rocks: igneous, sedimentary and metamorphic (Jonasson and Boyle 1979). Cinnabar (HgS) is the most common mercury ore (Jonasson and Boyle 1971; Vostal 1972; McNeely *et al.* 1979). Mercury, however, is present in more than 30 common ore and gangue minerals (Jonasson and Boyle 1972). Prominent examples include the sulphide minerals tetrahedrite ($Cu_{12}Sb_4S_{13}$), sphalerite (ZnS) and wurtzite ((Fe,Zn)S) (Jonasson and Boyle 1979).

Mercury is also present in the atmosphere as metallic mercury vapours and as volatilized organic mercury compounds (Health and Welfare Canada 1980). Terrestrial environments appear to be major sources of atmospheric mercury, with contributions from evapotranspiration of leaves, decaying vegetation and degassing of soils (Kothny 1973). Volcanic, fumarolic and thermal spring activities probably make only small contributions on a global basis (Jonasson and Boyle 1979). Organomercurials may enter the atmosphere through microbial, plant or animal metabolic activity (Health and Welfare Canada 1980); possibly from geothermal sites (Jepsen 1973); and as a result of soil degassing (Rogers 1975). Atmospheric mercury can enter terrestrial and aquatic habitats via particle deposition and precipitation (Wallace *et al.* 1971; Jonasson and Boyle 1979; Health and Welfare Canada 1980).

The annual amount of mercury estimated to enter the ecosystem on a global basis is 44 230 t, about 80% of which comes from natural sources (Lagerwerff 1972). The remaining 20% comes from anthropogenic sources. A more recent report estimates a global mercury discharge of 1300 t each year to water from natural sources (NAS 1977). Anthropogenic sources can, however, be more ecologically significant than natural sources in given local regions (Reeder *et al.* 1979). Canadian mercury emissions to the atmosphere in 1978 were estimated at 39.9 t (Table 6-28). Base metal recovery accounted for 40.8%; coal combustion, 12.7%; paint application, 12%; and the chlor-alkali industry, 6% of the total emissions in that year (Sheffield 1983). These estimated mercury emissions approached the estimated annual mercury release from natural processes (30-50 t) in Canada (Environment Canada 1973).

Table 6-28. Anthropogenic Sources of Mercury in the Aquatic Environment

Source	Amount (t)
Direct discharge	
Mercury-cell chlor-alkali plants	0.450
Various mining and smelting processes	NA[1]
Aqueous effluent from sewage treatment facilities	NA
Manufacture of certain consumer products	NA
Emissions to atmosphere	
Mercury-cell chlor-alkali plants	2.374
Open burning at municipal dumps and sanitary landfill sites from discarded electrical components	1.623
Freshly painted surfaces	4.770
Sewage sludge incineration	0.124
Combustion of coal	5.042
oil	2.735
natural gas	0.517
wood	0.767
Fluorescent tube breakage	3.375
Thermometer breakage	0.403
Base metal recovery	16.270
Agricultural chemicals	1.103
Paint manufacture	0.065
Pharmaceutical use	0.236
Mercury-containing instruments	0.244
Other	0.272
Groundwater[2]	
Discarded electrical components at municipal dumps and sanitary landfill sites	NA
Disposal sites for sewage sludge	NA

[1] NA = not available.

[2] Amount, though not stated, is not significant (except in localized areas) because of uptake by plants and sorption to soil particles (NRCC 1979).

Sources: NRCC 1979; Sheffield 1983.

6.2.26.3 Environmental Concentrations

The overall terrestrial abundance of mercury appears to be in the order of 0.05 $mg \cdot kg^{-1}$. Ore currently considered as an economic deposit is usually found in limestone or sandstone at levels of 0.5-6% mercury by weight (Jonasson and Boyle 1979). Ores from British Columbia contain about 0.2% recoverable mercury (Vostal 1972).

Background concentrations of inorganic mercury in air are approximately 0.5 $ng \cdot m^{-3}$, whereas concentrations of 1500-9000 $ng \cdot m^{-3}$ may be found in the vicinity of mercury deposits and active volcanoes (NRCC 1979).

Provincial median values measured in Canadian drinking water range from 0.15 to 0.29 $\mu g \cdot L^{-1}$ (NAQUADAT 1976). The natural levels of mercury in Canadian surface waters vary from area to area, and are usually close to the detection limit (0.05 $\mu g \cdot L^{-1}$) (Reeder *et al.* 1979). In the Great Lakes, mean mercury concentrations were found to range from 0.13 to 0.18 μg·L^{-1} (Chau and Saitoh 1973), except for Lake Michigan which contained mercury at 0.27 μg·L^{-1} (Klein 1975). Values up to 30 μg·L^{-1} have been found in the St. Clair River near Windsor, Ontario (U.S. Department of the Interior 1970). Streams and rivers near mercury deposits may contain up to 100 μg·L^{-1} (Reeder *et al.* 1979). One study has shown typical oceanic values for mercury to be 0.01-0.03 μg·L^{-1}, whereas freshwater values vary between 0.02 and 0.06 μg·L^{-1} (NAS 1977). In Minamata Bay, Japan, an area seriously affected by mercury pollution, values ranged from 1.6 to 3.6 μg·L^{-1} (U.S. EPA 1980).

Environmental concentration ranges for mercury in Canadian surface waters are presented in Table 6-29.

The content of mercury in sediments is highly variable. The lowest values (1 ng·g^{-1}) are found in the sand fraction. The highest mercury levels are generally found in sediments rich in organic materials (Reeder *et al.* 1979).

The form of mercury most commonly found in fish is methylmercury (NRCC 1979). In Canadian inland natural waters, fish usually have total mercury contents below 0.5 μg·g^{-1} (wet weight) (Reeder *et al.* 1979). Elevated mercury contents (2.73-10.5 μg·g^{-1}) have been found in Canadian freshwater fish taken from areas suspected of mercury contamination (Fimreite 1970), and at least some fish sampled from Lake Erie were found to have tissue levels exceeding 0.5 μg·g^{-1} (Health and Welfare Canada 1980). In other Great Lakes and inland locations unaffected by known mercury discharges, the mercury concentrations are usually higher in predatory fish (Ontario Ministry of the Environment 1985).

Table 6-29. Environmental Concentration Ranges for Mercury in Canadian Surface Waters

Region	Concentration range (μg·L^{-1})	Number of samples	Sampling year(s)
Pacific	<0.05[1]	141	1980-1982
Western	<0.02-0.24[1]	223	1980-1983
Central	0.005-0.100	622	1980-1981

[1] Detection limit is 0.05 μg·L^{-1}.

Source: NAQUADAT 1985.

6.2.26.4 Forms and Fate in the Aquatic Environment

Mercury can exist in three oxidation states in the natural environment: elemental, mercurous Hg(I) and mercuric Hg(II) (Jonasson and Boyle 1979; U.S. EPA 1979). The chemical speciation of mercury depends on redox potential, pH and the type of ligands present (U.S. EPA 1979; Ramamoorthy and Massalski 1979). On the basis of thermodynamic data, mercury may form numerous soluble species; some of these complex ions have appreciable aqueous solubility, whereas others are quite insoluble. In deionized water under moderately oxidizing conditions above pH 5, the predominant species present is elemental mercury. Alternatively, in natural waters containing micro- and macrosolutes which may be potential ligands for mercury, Hg(II) is expected to predominate at low redox potential (Ramamoorthy and Massalski 1979). Under mildly reducing conditions, mercury will be in the form of the insoluble sulphide. Mercury exhibits a strong affinity for both sulphydryl and amino groups, and undergoes alkylation to yield alkylated mercury compounds, such as monomethyl- and dimethylmercury, in the aquatic environment (U.S. EPA 1979). Dimethylmercury is water-soluble, and has a predicted half-life in water at pH 5 and 25°C of approximately 33 years (Wolfe *et al.* 1973; Zepp *et al.* 1974). It has a higher volatility than monomethylmercury, and, hence, loss from surface water because of volatilization will be greater and will depend upon such factors as turbulence, mixing and wind speed. Monomethylmercury is likely to be complexed as sulphur-bonded compounds. In the absence of organic matter, methyl-mercuric hydroxides and chlorides would predominate (Wasik *et al.* 1976). Both the mono- and dimethyl forms have a high affinity for biotic tissues and are readily taken up by organisms, with the monomethyl form undergoing more rapid membrane transport (Jensen and Jernelov 1969).

Mercury concentrations in true aqueous solution are relatively small (Pecora 1970; McNeely *et al.* 1979; Reeder *et al.* 1979). In freshwater habitats, it is common for mercury compounds to be sorbed to particulate matter and to sediment (Wallace *et al.* 1971; McNeely *et al.* 1979). In fact, Hg(II) sorption onto sediments is probably the most important process for determining its abiotic fate in the aquatic environment (U.S. EPA 1979). Sediment binding capacity is related to organic content, and appears to be little affected by pH. In addition, sediment desorption rates are low (Ramamoorthy and Rust 1976). Mercury tends to combine with sulphur in anaerobic bottom sediments (Yamada and Tonomura 1972; McNeely *et al.* 1979). Elemental mercury, being volatile, may be transferred to the atmosphere (U.S. EPA 1979). The rate of volatilization of inorganic mercury compounds decreases as $Hg^{\circ} > Hg_2Cl_2 > HgCl_2 > HgS > HgO$ (U.S. EPA 1979). The biological methylation of mercury could also enhance its evaporative loss. Although photodegradation of phenylmercury compounds has been demonstrated in water, it is not clear whether photolysis plays an important role in mercury removal from the water column (U.S. EPA 1979).

Mercury(II) ion can be transformed into mono- and dimethylmercury by the action of microorganisms under both aerobic and anaerobic conditions (Bisogni and Lawrence 1975; Wood 1976; McNeely *et al.* 1979). Bacteria common to most natural waters are capable of this action (Jensen and Jernelov 1969; Bisogni and Lawrence 1975). Low concentrations of inorganic mercury and a high pH favour the formation of dimethylmercury, whereas higher concentrations under acidic conditions favour the formation of monomethylmercury (Bisogni and Lawrence 1975; McNeely *et al.* 1979). The amounts of mono- and dimethylmercury are influenced by the presence of microbial flora, organic carbon concentrations, inorganic mercury concentrations, pH and temperature (Bisogni and Lawrence 1975; McNeely *et al.* 1979; U.S. EPA 1979). Both forms of methylmercury may also be demethylated by bacteria in sediments (Fagerstrom and Jernelov 1972; NAS 1977; McNeely *et al.* 1979; Ramamoorthy *et al.* 1982).

Even though most of the mercury present in the water column is in the divalent inorganic form, methylated forms constitute most of the mercury residues in the tissues of aquatic organisms (IJC 1977; Hattula *et al.* 1978). Bioconcentration factors for aquatic organisms are usually high (~10^4), because of rapid uptake and slow depuration. The biological half-life for mercury in fish is estimated to be approximately 2 years (Lockhart *et al.* 1972; McKim *et al.* 1976). Lower pH values in the water column generally increase mercury solubility, rate of methylation and rate of uptake. For example, within the pH range of 4.5-6.5, a 0.5-unit decrease in pH corresponds to an increase of 0.025 $mg \cdot kg^{-1}$ in mercury residues in resident fish (Jernelov 1980). Aquatic organisms may accumulate methylmercury either directly from water or through the food web (Phillips and Russo 1978; U.S. EPA 1979; McNeely *et al.* 1979). Predators achieve higher concentrations than do organisms lower in the food web. In Canadian fresh waters, high concentrations of mercury have been found in lake trout, pike and walleye (NRCC 1979).

6.2.26.5 References

Bisogni, J.J., Jr. and A.W. Lawrence. 1975. Kinetics of mercury methylation in aerobic and anaerobic aquatic environments. J. Water Pollut. Control Fed. 47: 135-152.

Chau, Y.K. and H. Saitoh. 1973. Mercury in the international Great Lakes. *In* Proc. 16th Conf. on Great Lakes Research, April 16-18, Huron, Ohio. pp. 221-232.

Environment Canada. 1973. National Inventory of Sources and Emissions of Mercury (1970). Air Pollution Control Directorate, Environmental Protection Service. Intern. Rep. APCD 73-6.

Fagerstrom, T. and A. Jernelov. 1972. Some aspects of the quantitative ecology of mercury. Water Res. 6: 1193-1202.

Fimreite, N. 1970. Mercury uses in Canada and their possible hazards as sources of mercury. Environ. Pollut. 1: 119-131.

Hattula, M.L., J. Sarkka, J. Janatuinen, J. Paasivirta and A. Roos. 1978. Total mercury and methylmercury contents in fish from Lake Paijanne. Environ. Pollut. 17: 19-39.

Health and Welfare Canada. 1980. Mercury. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 387-407.

Hocking, M.B. 1979. Uses and emissions of mercury in Canada. *In* Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. pp. 50-75.

Hogan, J.J. 1983. Mercury. *In* Canadian Minerals Yearbook 1980. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report No. 30.

IJC: 1977. Mercury. *In* New and Revised Great Lakes Water Quality Objectives. Vol. II. A Report to the Governments of the United States and Canada, International Joint Commission, Windsor, Ontario. pp. 74-80.

Jensen, S. and A. Jernelov. 1969. Biological methylation in aquatic organisms. Nature (London) 223: 753-754.

Jepsen, A.F. 1973. Measurements of mercury vapor in the atmosphere. *In* Trace Elements in the Environment. E.L. Kothny (ed.). Adv. Chem. Ser. No. 123. pp. 81-95. (Cited in Jonasson and Boyle 1979.)

Jernelov, A. 1980. The effects of acidity on the uptake of mercury in fish. Environ. Sci. Res. 17: 211-222.

Jonasson, I.R. and R.W. Boyle. 1971. Geochemistry of mercury. *In* Proc. Special Symp. on Mercury in Man's Environment, The Royal Society of Canada, Feb. 15-16, Ottawa. pp. 5-21. (Cited in Jonasson and Boyle 1979.)

Jonasson, I.R. and R.W. Boyle. 1972. Geochemistry of mercury and origins of natural contamination of the environment. Can. Min. Metall. Bull. 65(717): 32-39.

Jonasson, I.R. and R.W. Boyle. 1979. The biogeochemistry of mercury. *In* Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. pp. 28-49.

Klein, D.H. 1975. Fluxes, residence times and sources of some elements to Lake Michigan. Water Air Soil Pollut. 4: 3-8.

Kothny, E.L. 1973. The three-phase equilibrium of mercury in nature. *In* Trace Elements in the Environment. E.L. Kothny (ed.). Adv. Chem. Ser. No. 123. pp. 48-80. (Cited in Jonasson and Boyle 1979.)

Lagerwerff, J.V. 1972. Lead, mercury and cadmium as environmental contaminants. *In* Micronutrients in Agriculture. Soil Science Society of America Inc., Madison, Wisconsin. p. 609.

Lockhart, W.L., J.F. Uthe, A.R. Kennedy and P.H. Mehrle. 1972. Methylmercury in northern pike (*Esox lucius*): distribution, elimination and some biochemical characteristics of contaminated fish. J. Fish. Res. Board Can. 29: 1519-1523.

McKim, J.M., G.F. Olson, G.W. Holcombe and E.P. Hunt. 1976. Long-term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): Toxicity, accumulation, distribution and elimination. J. Fish. Res. Board Can. 33: 2726-2739.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Mercury. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 23-24.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. (Data for the period 1960-1976.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. An Assessment of Mercury in the Environment. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NRCC. 1979. Effects of Mercury in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16739. 290 pp.

Ontario Ministry of the Environment. 1985. Guide to Eating Ontario Sport Fish. Toronto, Ontario.

Pecora, W.T. 1970. Mercury in the Environment. U.S. Geol. Surv. Prof. Pap. No. 713. 67 pp. (Cited in Jonasson and Boyle 1979.)

Phillips, G.R. and R.C. Russo. 1978. Metal Bioaccumulation in Fishes and Aquatic Invertebrates. U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, Minnesota. EPA-600/3-78-103.

Ramamoorthy, S. and A. Massalski. 1979. Analysis of structure-localized mercury in Ottawa River sediments by scanning electron microscopy/energy-dispersive X-ray microanalysis technique. Environ. Geol. 2: 351-357.

Ramamoorthy, S. and B.R. Rust. 1976. Mercury sorption and desorption characteristics of some Ottawa River sediments. Can. J. Earth Sci. 13: 530-536.

Ramamoorthy, S., T.C. Cheng and D.J. Kushner. 1982. Effect of microbial life stages on the fate of methylmercury in natural waters. Bull. Environ. Contam. Toxicol. 29: 167-173.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979. Mercury. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rogers, R.D. 1975. Methylation of mercury in a terrestrial environment. U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-75-014.

Sheffield, A. 1983. National Inventory of Sources and Emissions of Mercury (1978). Environmental Protection Service, Environment Canada, Ottawa. Economic and Technical Review Rep. EPS 3-AP-81-1.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. Department of the Interior. 1970. Investigations of mercury in the St. Clair River-Lake Erie systems. Report of the Federal Water Quality Administration. National Field Investigations Center, Cincinnati, Ohio. p. 108. (Cited in Health and Welfare Canada 1980.)

U.S. EPA. 1979. Mercury. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 14-1 to 14-15.

U.S. EPA. 1980. Ambient Water Quality Criteria for Mercury. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-058.

Vostal, J. 1972. Transport and transformation of mercury in nature and possible routes of exposure. *In* Mercury in the Environment. L. Friberg and J. Vostal (eds.). CRC Press, Cleveland, Ohio. pp. 15-27.

Wallace, R.A., W. Fulkerson, W.D. Shields and W.S. Lyons. 1971. Mercury in the Environment: the Human Element. Oak Ridge National Laboratory, Oak Ridge, Tennessee. Rep. No. ORNL-NSF-EP-1. 61 pp. (Cited in Jonasson and Boyle 1979.)

Wasik, S.P., R.L. Brown and J.J. Minor. 1976. Partition coefficients and solubility measurements of dimethylmercury in fresh and sea water over a temperature range of 0-25°C. J. Environ. Sci. Health Part A 1: 99-105.

Wolfe, N.L., R.G. Zepp, J.A. Gordon and G.L. Baughman. 1973. Chemistry of methyl mercurials in aqueous solution. Chemosphere 4: 147-152.

Wood, J.M. 1976. Les métaux toxiques dans l'environnement. Recherche 7: 711. (Cited in U.S. EPA 1980.)

Yamada, M. and K. Tonomura. 1972. Formation of mercury compounds from inorganic mercury by *Clostridium cochlearum*. J. Ferment. Technol. 50: 159-166. (Cited in Jonasson and Boyle 1979.)

Zepp, R.G., G.L. Baughman, N.L. Wolfe and D.M. Cline. 1974. Methyl mercury complexes in aquatic systems. Environ. Lett. 6: 117-127.

6.2.27 Molybdenum

6.2.27.1 Uses and Production

Molybdenum is used in the manufacture of special steel alloys and electronic apparatus. Molybdenum salts are used in the manufacture of glass, ceramics, pigments and fertilizers (McNeely *et al.* 1979). Commercial deposits of molybdenum contain 200 mg·kg^{-1} or more; lower concentrations are generally recovered as a by-product of copper mining. World production in 1975 was estimated at 7.5 × 10^6 t (Chappell 1975). Production, consumption, importation and exportation data for molybdenum in Canada are presented in Table 6-30.

6.2.27.2 Sources and Pathways for Entering the Aquatic Environment

Molybdenum is widely distributed in nature, occurring chiefly as molybdenite (MoS_2) and molybdates (MoO_4^{2-}). The weathering of igneous and sedimentary rocks (especially shales) constitutes an important natural source of molybdenum to the aquatic environment (Chappell 1975).

Mining and milling of molybdenum, the use of molybdenum products, the mining and milling of some uranium and copper ores and the burning of fossil fuels may also contribute molybdenum to the aquatic environment (Chappell 1975). The use of fertilizers containing molybdenum, however, provides the single most important anthropogenic input to the aquatic environment (McNeely *et al.* 1979).

6.2.27.3 Environmental Concentrations

Fresh water usually contains less than 1 mg·L^{-1} molybdenum, whereas seawater contains less than 0.01 mg·L^{-1} (McNeely *et al.* 1979). Concentrations of molybdenum in fresh water range from approximately 0.03 to 10 μg·L^{-1} (Cowgill 1977; Bowen 1979).

Table 6-30. Production, Consumption, Importation and Exportation of Molybdenum in Canada

Parameter	Amount (t)		
	1982	1983	1984
Production	13 961	10 194	10 965
Consumption	671 368	490 117	NA[1]
Importation	3 297	408	371[2]
Exportation	17 443	11 284	6 349

[1] NA = not available.

[2] Partial estimate only.

Source: Fong 1985.

A study conducted near Dauphin, Manitoba, reported that sediment molybdenum concentrations were generally below 3 μg·g^{-1}, but concentrations as high as 14 μg·g^{-1} were reported in a few sample sites where soils associated with these sediments were at pH 5.1. Shale formations in the same study leached molybdenum into the surrounding soils, where concentrations were as high as 20 μg·g^{-1} (Doyle and Fletcher 1977). Average concentrations of molybdenum (total) in NAQUADAT were reported to be 1 μg·L^{-1} (detection limit 0.2 μg·L^{-1}) for 293 samples taken prior to 1980 in the Central region of Canada. Only one NAQUADAT station reported a molybdenum (total) concentration after 1980; the station, located on a river in Quebec, reported a molybdenum (total) concentration of 1.0 μg·L^{-1} (detection limit 0.2 μg·L^{-1}) in 1981 (NAQUADAT 1985).

6.2.27.4 Forms and Fate in the Aquatic Environment

Molybdenum occurs in oxidation states of +2, +3, +4, +5 and +6; the tetravalent and hexavalent states predominate in nature (Jarrell *et al.* 1980). Several organometallic molybdenum compounds are also known (Cotton and Wilkinson 1980). Molybdenum may occur in natural waters in the +4 oxidation state as molybdenum sulphide (MoS_2) and in the +6 oxidation state as the molybdate anion (MoO_4^{2-}). Molybdenum sulphide is sparingly soluble in water and is fairly readily oxidized to soluble molybdates, which are stable in aerobic waters (Cotton and Wilkinson 1980).

Dissolved molybdenum in natural waters occurs mainly as molybdate (MoO_4^{2-}) and bimolybdate ($HMoO_4^-$) anions (Jones 1957). Adsorption and coprecipitation of the molybdate anion by hydrous oxides of iron and aluminum play primary roles in determining the aquatic fate of molybdenum (Allaway 1977). Ferric oxyhydroxides readily adsorb molybdenum; the optimal removal of dissolved molybdenum occurs at pH 3-4 in the presence of a 10-fold excess of iron (Jones 1957; LeGrande and Runnells 1975). Hydrous aluminum oxides also adsorb molybdenum. Maximum sorption occurs at pH 4.8 (Jones 1957), although much higher concentrations of aluminum relative to molybdenum are required (LeGrande and Runnells 1975). Above pH 5, the influence of sorption decreases, and molybdenum in natural waters is essentially dissolved (LeGrande and Runnells 1975). As redox potential is lowered, the solubility of molybdenum increases. A reduction from ferric to ferrous iron, accompanied by an increased dissolution of ferric molybdate, may be involved in enhanced solubility at low redox potential (Allaway 1977). Sorption to surfaces decreases in the order ferric oxide > aluminum oxide > halloysite > nontorite > kaolinite (Jones 1957). Laboratory experiments have indicated that the concentration of molybdenum released to the water column also depends upon grain size of the sediment; generally, as grain size decreases, the concentration in the water column decreases, indicating a greater bulk sorption. In addition, a weak positive correlation was found between molybdenum concentration and organic matter content in natural sediments (Runnells *et al.* 1977).

Molybdenum is considered to be essential to nitrogen-fixing plants and in certain oxidation-reduction enzyme systems (Venugopal and Luckey 1978). In aerobic seawater, sulphate has been found to inhibit the assimilation of molybdenum by phytoplankton (Howarth and Cole 1985). Molybdenum has been found to be accumulated in numerous aquatic organisms, such as algae (0.3-2 mg·kg^{-1}), vascular plants (0.3-5 mg·kg^{-1}) and the soft tissues of fish (1 mg·kg^{-1}), in fresh water at low concentrations (0.03-10 μg·L^{-1}) (Cowgill 1977; Bowen 1979). Concentration factors of 10^3 have been found in freshwater plankton and sediments (Groth 1971; Wetzel 1975).

6.2.27.5 References

Allaway, W.H. 1977. Perspectives on molybdenum in soils and plants. *In* Molybdenum in the Environment. Vol. 2. W.R. Chappell and K.K. Petersen (eds.). Marcel Dekker, Inc., New York. pp. 317-339.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, Toronto, Ontario. 333 pp.

Chappell, W.R. 1975. Transport and biological effects of molybdenum in the environment. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Oxford. pp. 167-188.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Cowgill, U.M. 1977. The molybdenum cycle in Linsley Pond, North Branford, Connecticut. *In* Molybdenum in the Environment. Vol. 2. W.R. Chappell and K.K. Petersen (eds.). Marcel Dekker, Inc., New York. pp. 705-723.

Doyle, P.J. and K. Fletcher. 1977. Molybdenum content of bedrock, soils and vegetation and the incidence of copper deficiency in cattle in western Manitoba. *In* Molybdenum in the Environment. Vol. 2. W.R. Chappell and K.K. Petersen (eds.). Marcel Dekker, Inc., New York. pp. 371-386.

Fong, D.G. 1985. Molybdenum. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 42.1-42.11.

Groth, P. 1971. Untersuchungen über einige Spurenlemen. *In* Seen. Arch. Hydrobiol. 68: 305-373. (Cited in Wetzel 1975.)

Howarth, R.W. and J.J. Cole. 1985. Molybdenum availability, nitrogen limitation, and phytoplankton growth in natural waters. Science 229: 653-655.

Jarrell, W.M., A.L. Page and A.A. Elseewi. 1980. Molybdenum in the environment. Residue Rev. 74: 1-43.

Jones, L.H.P. 1957. The solubility of molybdenum in simplified systems and aqueous soil suspensions. J. Soil Sci. 8: 312-327.

LeGrande, G.R. and D.D. Runnells. 1975. Removal of dissolved molybdenum by precipitation of ferric iron. Environ. Sci. Technol. 9: 744-749.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Molybdenum. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 24.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Runnells, D.D., D.S. Kaback and E.M. Thurman. 1977. Geochemistry and sampling of molybdenum in sediments, soils and plants in Colorado. *In* Molybdenum in the Environment. Vol. 2. W.R. Chappell and K.K. Petersen (eds.). Marcel Dekker., Inc., New York. pp. 387-423.

Venugopal, B. and T.D. Luckey. 1978. Metal Toxicity in Mammals. Vol. 2. Plenum Press, New York.

Wetzel, R.G. 1975. Limnology. W.B. Saunders and Co., Philadelphia, Pennsylvania. 743 pp.

6.2.28 Nickel

6.2.28.1 Uses and Production

The uses of nickel are based on its resistance to corrosion, high strength over a wide temperature range, good alloying properties and good appearance. Nickel can be drawn, rolled, forged and polished (Taylor *et al.* 1979).

The manufacture of stainless steel, nickel plating and high-nickel alloys constitutes the main uses of nickel. High-nickel alloys are used in chemical, marine, electronic, nuclear and aerospace applications. Nickel is also used as a catalyst in industrial processes and in oil refining. More recently, it has been used in nuclear generating plants, gas turbine engines, cryogenic containers and pollution abatement equipment (Taylor *et al.* 1979; McNeely *et al.* 1979).

Production, consumption, importation and exportation data for nickel in Canada are presented in Table 6-31.

6.2.28.2 Sources and Pathways for Entering the Aquatic Environment

Nickel ranks as the 23rd element in order of abundance in the earth's crust, and occurs in nature mainly in combination with sulphur, arsenic and antimony. Its average concentration in the earth's crust is 75 mg·kg^{-1} (Taylor 1964). The concentration of nickel ranges from 1 mg·kg^{-1} in sandstone (sedimentary rock) to 160 mg·kg^{-1} in basalt and gabbro to 2000 mg·kg^{-1} and more in peridotites and durites (NAS 1975). Most nickel is produced from sulphide ores, such as pentlandite ($(Fe,Ni)_9S_8$), in which it occurs mainly with iron and copper. Other types of nickel deposits are the oxide ores, such as garnierite ($(Ni,Mg)_6[(OH)_6Si_4O_{11}]H_2O$) and limonite ($(Ni,Fe)O(OH)\cdot nH_2O$). Pentlandite is found in Sudbury, Ontario, at one of the world's largest deposits of nickel (Taylor *et al.* 1979). In 1975, Canada accounted for 34% of the total world nickel production. The arsenide ores, such as niccolite (NiAs), chloanthite ($NiAs_2$) and nickel glance (NiAsS), which also occur in Canada, are of less importance (Nicholls 1973).

Nickel enters the environment primarily through the weathering of minerals and rocks, and as a result of human activities. The global loading of nickel to the aquatic environment is approximately 160 000 t·a^{-1} as a result of the weathering process. Approximately 7% of this total is in the dissolved phase, and the rest is in particulate form. The other potential natural source is volcanic activity, but its contribution would not be expected to be significant relative to anthropogenic emissions (Bertine and Goldberg 1971).

Table 6-31. Production, Consumption, Importation and Exportation of Nickel in Canada

Parameter	Amount (t)		
	1982	1983	1984
Production	88 581	121 836	174 195
Consumption	6 637	5 015	NA[1]
Importation (nickel ore and all nickel products)	29 145	34 811	22 024
Exportation (nickel ore and all nickel products)	116 156	131 556	132 658

[1] NA = not available.

Source: Telewiak 1985.

Table 6-32. Environmental Concentration Ranges for Nickel in Canadian Surface Waters

Region	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<1[1]-3	10	1982
Western	1[2]-280	1625	1980-1985
Central	1[1]-25	1333	1980-1985
Atlantic	1[1]-3	70	1980-1983

[1] Detection limit is 1 $\mu g \cdot L^{-1}$ (total).

[2] Detection limit is 2 $\mu g \cdot L^{-1}$ (total recoverable).

Source: NAQUADAT 1985.

The major contributor of nickel released to the environment by human activity is the burning of fossil fuels. Nickel concentrations in crude oil range from 0.6 $mg \cdot kg^{-1}$ to more than 300 $mg \cdot kg^{-1}$ (Demayo *et al.* 1979); using an average nickel concentration of 10 $mg \cdot kg^{-1}$ and a global oil consumption (in 1974) of 2.743×10^9 t, the calculated amount of nickel released would be approximately 27 000 t. About 10% of this amount enters the atmosphere (Bertine and Goldberg 1971). In 1974, about 22 500 t of nickel originated from burned coal. The total world emission of nickel to the atmosphere in 1974 is estimated at 5985 t, of which 5151 t were released through combustion of coal and oil (Sittig 1975).

Nickel ore mining, smelting and refining of concentrates, smelting and casting of alloys and electroplating industries are also major contributors to the release of nickel to the environment. Two samples taken in 1982 from a British Columbia industrial wastewater station of NAQUADAT had a total nickel concentration below 1 $\mu g \cdot L^{-1}$ (detection limit) (NAQUADAT 1985). Nickel is also released from the manufacture of foods, baked goods, soft drinks, flavouring syrups and ice cream (Taylor *et al.* 1979).

6.2.28.3 Environmental Concentrations

Nickel concentrations as high as 0.10 $mg \cdot L^{-1}$ have been found in natural surface waters, and concentrations as high as 11 $mg \cdot L^{-1}$ have been detected in mining areas (NAS 1975).

Environmental concentration ranges for nickel in Canadian surface waters are presented in Table 6-32.

Nickel concentrations in sediment from the Ottawa River in 1974 were between 1 and 85 $mg \cdot kg^{-1}$ (mean 26 $mg \cdot kg^{-1}$), and in sediment from the Rideau River (Ottawa) concentrations ranged from nondetectable levels to 135 $mg \cdot kg^{-1}$ (mean 22 $mg \cdot kg^{-1}$). In lake sediments near mining operations (silver, copper) in the Northwest Territories, much higher values, e.g. 190-1050 $mg \cdot kg^{-1}$, have been found (Oliver and Agemian 1974).

Data on drinking water from 233 localities in Canada show that average nickel concentrations range from 2.9 to 7.2 $\mu g \cdot L^{-1}$. Nickel is absent in most groundwaters (Neri 1976).

6.2.28.4 Forms and Fate in the Aquatic Environment

Nickel may occur in oxidation states ranging from −1 to +4 in aqueous systems; however, it occurs predominantly in the divalent state. The chemistry of nickel in aqueous solutions is essentially that of the divalent cation (Cotton and Wilkinson 1980). Nickel(II) halides and other simple salts form a large number of complexes with ligands with nitrogen and phosphorus donor atoms (Nicholls 1973).

Nickel occurs in aqueous systems as relatively soluble salts associated with suspended solids and in combination with organic material. It is also found in aquatic sediments and biota (NRCC 1981). Under anaerobic conditions and in the presence of sulphur, insoluble sulphides are formed. However, under aerobic conditions below pH 9.0, nickel will form compounds with hydroxide, carbonate, sulphate and organic ligands. No direct chemical speciation techniques have been successfully developed for nickel, although numerous laboratory studies utilizing equilibrium data have been conducted (NRCC 1981). Nickel sorption to various sorbents, including iron and manganese oxides and silica, have been studied. In general, above pH 6.0, nickel is sorbed to iron and manganese oxides, and its soluble complex species decrease in concentration (Richter and Theis 1980). Nickel has been shown to coprecipitate with iron and manganese oxides (Lee 1975) and sorb to suspended organic matter (Rashid 1974). Although concentrations in sediment are usually higher than those in water, nickel is considered to be highly mobile in aqueous systems, with sorption playing a relatively minor role in water below pH 6.0 (U.S. EPA 1979; NRCC 1981). Under aerobic conditions and in the presence of microorganisms, nickel can be remobilized from sediments (Stokes and Szokalo 1977).

There is no evidence to suggest that either photolysis or volatilization of nickel compounds plays an important role in removing nickel from the water column (U.S. EPA 1979).

Nickel is bioaccumulated by some aquatic organisms; concentration factors, in general, are in the order of 10^2-10^4 for freshwater algae and macrophytes and 10^2 for zooplankton, clams and fish (Chapman *et al.* 1968; Dietz 1973; Hutchinson and Stokes 1975). Studies with freshwater fauna indicated the absence of biomagnification through the food web. In general, bioconcentration factors are highest in aquatic plants, intermediate in invertebrates and lowest in fish (Hutchinson *et al.* 1975). A biological half-life of 71 d was found for trout (*Salmo gairdneri*) muscle (Calamari *et al.* 1982).

6.2.28.5 References

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Calamari, D., G.F. Gaggino and G. Pacchetti. 1982. Toxicokinetics of low levels of Cd, Cr, Ni, and their mixture in long-term treatment on *Salmo gairdneri* Rich. Chemosphere 11: 59-70.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Demayo, A., E. Brien and K.W. Taylor. 1979. Elemental Composition of Fossil Fuels and their Ashes. A Review. Unpublished Report. Water Quality Branch, Environment Canada, Ottawa.

Dietz, F. 1973. The enrichment of heavy metals in submerged plants. *In* 6th Int. Conf. Adv. Water Pollut. Res., 1972, Jerusalem. pp. 53-62. (Cited in Taylor *et al.* 1979.)

Hutchinson, T.C. and P.M. Stokes. 1975. Heavy metal toxicity and algal bioassays. ASTM Spec. Tech. Publ. No. 573. pp. 320-343.

Hutchinson, T.C., A. Fedorenko, J. Fitchko, A. Kuja, J. Van Loon and J. Lichwa. 1975. Movement and compartmentation of nickel and copper in an aquatic ecosystem. *In* Environmental Biogeochemistry. Vol. 2. Metals Transfer and Ecological Mass Balances. J.O. Nriagu (ed.). Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Oxford. pp. 137-149.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Nickel. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 24-25.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1975. Nickel. Medical and Biologic Effects of Environmental Pollutants. Division of Medical Sciences, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 277 pp. (Cited in Taylor *et al.* 1979.)

Neri, L.C. 1976. Some data from Canada. *In* Hardness of Drinking Water and Public Health. R. Amavis, W.J. Hunter and J.G.P.M. Smeets (eds.). Commission of the European Communities. Pergamon Press, Oxford. pp. 343-347. (Cited in Taylor *et al.* 1979.)

Nicholls, D. 1973. Nickel. *In* Comprehensive Inorganic Chemistry. Vol. 3. J.C. Bailar, H.C. Emeléus, Sir Ronald Nyholm and A.F. Trotman-Dickenson (eds.). Pergamon Press, New York. pp. 1109-1161.

NRCC. 1981. Effects of Nickel in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18568. 352 pp.

Oliver, B.G. and H. Agemian. 1974. Further Studies on the Heavy Metal Levels in Ottawa and Rideau River Sediments. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. Sci. Ser. No. 37.

Rashid, M.A. 1974. Adsorption of metals on sedimentary and peat humic substances. Chem. Geol. 13: 115-123.

Richter, R.O. and T.L. Theis. 1980. Nickel speciation in a soil/water system. *In* Nickel in the Environment. J.O. Nriagu (ed.). Wiley Interscience, New York. pp. 189-202.

Sittig, M. 1975. Environmental Sources and Emissions Handbook. Noyes Data Corporation, Park Ridge, New Jersey. (Cited in Taylor *et al.* 1979.)

Stokes, P.M. and A.M. Szokalo. 1977. Sediment-water interchange of copper and nickel in experimental aquaria. Water Pollut. Res. Can. 12: 157-177.

Taylor, M.C., A. Demayo and S.W. Reeder. 1979. Nickel. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285. (Cited in Taylor *et al.* 1979.)

Telewiak, R.G. 1985. Nickel. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 44-1 to 44-13.

U.S. EPA. 1979. Nickel. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 15-1 to 15-9.

6.2.29 Nitrogen

6.2.29.1 Introduction

Nitrogen occurs in the biosphere in oxidation states ranging from −3 (ammonia) to +5 (nitrate). Inorganic forms of nitrogen include nitrate (NO_3^-) and nitrite (NO_2^-), ammonia (NH_3) and molecular nitrogen (N_2). Several intermediate gaseous oxides of nitrogen are important in the atmosphere, but not in the aquatic environment. Naturally occurring organic nitrogen compounds containing amino and amide nitrogen, along with some heterocyclic compounds such as purines and pyrimidines, also occur in the aquatic environment (Brezonik 1972).

The major nitrogen species in the environment are interrelated by a complicated series of transformations that collectively comprise the nitrogen cycle. Although the biospheric nitrogen cycle is driven primarily by biologically mediated transformations, the atmospheric reactions of the cycle are chemical and photochemical in nature. In terrestrial and aquatic systems, the major abiotic processes involve phase transformations, such as volatilization, sorption and sedimentation (Brezonik 1972).

The biological transformation of nitrogen is composed of six major processes (see Figure 6-2) (Delwicke 1970; Brezonik 1972; Söderlund and Svensson 1976):

1. Assimilation of inorganic forms (primarily ammonia and nitrate) by plants and microorganisms to form organic nitrogen (e.g. amino acids, proteins). The dominant agents of assimilation in aquatic and terrestrial systems are autotrophic bacteria and higher plants (Lewin 1962; Bonner and Varner 1965; Stewart 1973).
2. Heterotrophic conversions, involving the transfer of organic nitrogen from one organism to another, are complicated (Brezonik 1972).

Table 6-33. Environmental Concentration Ranges for Nitrogen, Nitrite and Nitrate in Canadian Surface Waters

Parameter	Region	Concentration range ($mg \cdot L^{-1}$; dissolved)[1]	Number of samples	Sampling year(s)
Nitrogen ($NO_3 + NO_2$, $mg \cdot L^{-1}$ N, dl = 0.002 $mg \cdot L^{-1}$)	Pacific	0.002-3.60	1 417	1980-1983
	Central	0.002-1.820	2 713	1980-1983
Nitrogen ($NO_3 + NO_2$, $mg \cdot L^{-1}$ N, dl = 0.001 $mg \cdot L^{-1}$)	Pacific	<0.002-3.60	1 670	1980-1983
	Western	<0.001-190.0	31 319	Prior to 1980
	Central	<0.001-10.6	5 150	1980-1984
	Atlantic	<0.001-18.571	7 853	1980-1984
Nitrate ($mg \cdot L^{-1}$ N, dl = 0.023 $mg \cdot L^{-1}$)	Pacific	0.023-3.413	139	Prior to 1980
	Western	0.023-8.814	1 195	Prior to 1980
	Central	0.023-2.124	44	Prior to 1980
	Atlantic	0.023-1.320	540	1980-1984
Nitrate[2] ($mg \cdot L^{-1}$ N)	Pacific	0.002-6.60	389	Prior to 1980
	Central	0.002-69.30	524	Prior to 1980
	Atlantic	0.005-6.030	369	Prior to 1980
		0.50-10.60	25	1980-1984
Nitrate + nitrite[2] ($mg \cdot L^{-1}$ NO_3)	Western	0.01-2.20	211	Prior to 1980
	Atlantic	0.01-0.35	87	1980
Kjeldahl[2] (total, $mg \cdot L^{-1}$ N)	Pacific	0.014-20.0	5 545	Prior to 1980
	Western	0.148-2.630	21	1980-1981
	Central	0.004-31.70	2 582	1980-1983
	Atlantic	0.001-2.542	745	1980-1984
Organic nitrogen[2] (total, $mg \cdot L^{-1}$ N)	Pacific	0.05-0.10	3	Prior to 1980
	Atlantic	0.01-0.94	605	Prior to 1980

[1] Unless otherwise stated.

[2] Detection limit (dl) is not stated.

Source: NAQUADAT 1985.

3. Ammonification, the breakdown of organic nitrogen to ammonia, is carried out by bacteria and fungi in terrestrial and aquatic environments. The autolysis of cells and excretion of ammonia by zooplankton and fish are also important processes in aquatic systems (Brezonik 1972).
4. Nitrification, the microbial oxidation of ammonia to nitrite (NO_2^-) and nitrate (NO_3^-), is mediated primarily by aerobic bacteria (Focht and Verstraete 1977). The optimum pH for nitrification is approximately 8.0, with activity decreasing rapidly below pH 7. Nitrifying bacteria are mesophilic, preferring an optimum temperature of 30°C; the rate of nitrification is directly proportional to temperature. Nitrification can, however, occur even in cold climates. In the presence of high organic loading, the nitrification process can be inhibited (NAS 1978).

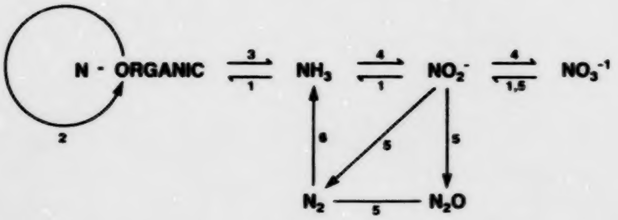


Figure 6-2. **Biological transformations of nitrogen (see text for explanation).**

5. Denitrification to produce nitrite as well as nitrous oxide (N_2O) and molecular nitrogen (N_2) may be mediated by numerous bacteria and fungi (Brezonik 1977). Nitrous oxide is the main product in sediments with a low but finite level of oxygen, whereas molecular nitrogen is the primary product in truly anaerobic sediments (Cady and Bartholomew 1960). Since denitrification is essentially an anaerobic process, its onset requires complete oxygen depletion, at least in the immediate environment of the microorganism. Denitrification can, however, occur at low oxygen levels, such as those found occurring in marshes, lake and stream sediments and waste treatment plants. The denitrification rate is directly proportional to temperature, and it may occur at temperatures ranging from less than 5 to 60°C. The optimum pH for biological activity is pH 7-8 (NAS 1978).
6. Biological nitrogen fixation involves the conversion of molecular nitrogen to ammonia, which in turn is directly incorporated into organic nitrogen compounds (NAS 1978). Numerous organisms may fix nitrogen, including blue-green algae and bacteria that live in association with macrophytes (Burns and Hardy 1975). As a group, nitrogen-fixing organisms are adapted to wide extremes in temperature, oxygen and pH, and can grow in harsh environments (NAS 1978).

Environmental concentration ranges for nitrogen, nitrite and nitrate for Canadian surface waters are presented in Table 6-33.

6.2.29.2 References

Bonner, J. and J.E. Varner. 1965. Plant Biochemistry. Academic Press, New York.

Brezonik, P.L. 1972. Nitrogen: sources and transformations in natural waters. *In* Nutrients in Natural Waters. H.E. Allen and J.R. Kramer (eds.). John Wiley & Sons, Toronto, Ontario. pp. 1-50.

Brezonik, P.L. 1977. Denitrification in natural waters. Prog. Water Technol. 8: 373-392.

Burns, R.C. and R.W.F. Hardy. 1975. Nitrogen Fixation in Bacteria and Higher Plants. Springer-Verlag, New York.

Cady, F.B. and W.V. Bartholomew. 1960. Sequential products of anaerobic denitrification in Norfolk soil material. Soil Sci. Soc. Am. Proc. 24: 477-482.

Delwiche, C.C. 1970. The nitrogen cycle. Sci. Am. 223: 137-146.

Focht, D.D. and W. Verstraete. 1977. Biochemical ecology of nitrification and denitrification. Adv. Microbial Ecol. 1: 135-214.

Lewin, R.A. 1962. Physiology and Biochemistry of Algae. Academic Press, New York.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1978. Nitrates: An Environmental Assessment. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 723 pp.

Söderlund, R. and B.H. Svensson. 1976. The global nitrogen cycle. *In* Nitrogen, Phosphorus and Sulfur – Global Cycles. SCOPE Report 7. B.H. Svensson and R. Söderlund (eds.). Ecological Bulletin No. 22. Swedish Natural Science Research Council, Stockholm, Sweden. pp. 23-73.

Stewart, W.D.P. 1973. Nitrogen fixation by photosynthetic microorganisms. Annu. Rev. Microbiol. 27: 283-318.

6.2.29.3 Ammonia

6.2.29.3.1 Uses and Production

The principal uses of synthetic ammonia are in agriculture (95%) for the production of urea, nitric acid, ammonium phosphates, ammonium nitrate, ammonium sulphate, fertilizer mixes and other fertilizer usage (Geadah 1985). Industrial uses of ammonia account for 4.3% and include mining/refining, pulp and paper and amines/nitriles production. Miscellaneous uses of ammonia account for only 0.7% of total production (Geadah 1985).

Canadian production and importation of ammonia and some of its compounds are presented in Table 6-34.

6.2.29.3.2 Sources and Pathways for Entering the Aquatic Environment

Ammonia (NH_3) is a colourless gas at ambient temperature and pressure, and has a distinct pungent odour (McKee and Wolf 1963; U.S. EPA 1976; Health and Welfare Canada 1980). Produced naturally by the biological degradation of nitrogenous matter (McKee and Wolf 1963; Luebs *et al.* 1973), it provides an essential link in the "nitrogen cycle" of nature (Delwiche 1973). Natural sources include biological litter, animal waste, forest fires and human breath (Geadah 1985).

Ammonia associated with clay minerals enters the aquatic environment through soil erosion. Bacteria associated with legumes, in particular, can fix large amounts of nitrogen in the soil; this nitrogen may be subsequently leached into surrounding waters (McNeely *et al.* 1979).

Commercial fertilizers contain highly soluble ammonia and ammonium salts. When the concentration of such compounds exceeds the immediate plant requirements, transport via the atmosphere or irrigation waters can carry these nitrogen compounds into the aquatic system (McNeely *et al.* 1979).

Table 6-34. Production and Importation of Ammonia and Ammonia Compounds in Canada

Compound	Amount (kt)	
	Production (year)	Importation (year)
Ammonia	3500 (1984)	41.2 (1983)
Ammonium chloride	None (since 1971)	3 (1979)
Ammonium nitrate	919 (1983)	10.32 (1982)
Ammonium phosphate	1376 (1983)	217.50 (1983)
Ammonium sulphate	206 (1983)	15.1 (1982)

Sources: CORPUS Information Services 1984, 1985.

Natural sources of ammonia include groundwater, gas exchange with the atmosphere, the chemical and biochemical transformation of nitrogenous organic and inorganic matter in soil and water, the excretion of ammonia by biota and the nitrogen fixation processes of dissolved nitrogen gas in water (Brezonik 1972).

Ammonia may be discharged from a wide variety of industrial cleaning operations that use ammonia or ammonium salts. Ammonia may also be discharged in municipal wastewaters. Explosives manufacturing and explosives use in mining and construction can also be significant sources of ammonia (Pommen 1983). Atmospheric deposition may contain significant amounts of ammonia (McNeely *et al.* 1979). Ammonia is released to the air through the distillation and combustion of coal and the biological degradation of manure (Robinson and Robbins 1968; Lund 1971; Luebs *et al.* 1973, 1974).

6.2.29.3.3 Environmental Concentrations

Ammonia is present in small amounts in air, water and soil, and in large amounts in decomposing organic matter (Geadah 1985). Natural waters typically contain ammonia and ammonium compounds in concentrations below 0.1 $mg{\cdot}L^{-1}$ (as nitrogen) (Klein 1959; McNeely *et al.* 1979). Higher concentrations may be an indication of anthropogenic input and organic pollution (Klein 1959; McNeely *et al.* 1979). Of 63 Canadian public water supplies surveyed between 1966 and 1974, 92% contained ammonia, measured as nitrogen, at concentrations of 0.2 $mg{\cdot}L^{-1}$ or less (NAQUADAT 1976).

Natural emissions of total ammonia to the atmosphere in Canada for 1980 have been estimated at 505 623 $t{\cdot}a^{-1}$ (Geadah 1985). Anthropogenic atmospheric emissions of ammonia in Canada have been estimated at 204 432 $t{\cdot}a^{-1}$, based on 1980 data (Geadah 1985).

Environmental concentration ranges for total ammonia in Canadian surface waters are presented in Table 6-35.

6.2.29.3.4 Forms and Fate in the Aquatic Environment

Ammonia, with an oxidation state of −3, is the reduced form of inorganic nitrogen in natural water. In aqueous solution, ammonia (un-ionized form) exists in equilibrium with ammonium ion (ionized form) according to the equation (Emerson *et al.* 1975):

$$NH_3(g) + H_2O \rightleftharpoons NH_3{\cdot}nH_2O(aq) \rightleftharpoons NH_4^+ + OH^- + (n-1)H_2O$$

Table 6-35. Environmental Concentration Ranges for Total Ammonia in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	<0.001-0.49	94	Prior to 1980
Western	0.014-2.00	1816	1980-1984
Central	0.005-0.587	13	1980-1983
Atlantic	0.002-0.104	346	1980-1981

[1] Detection limit is 1 μg·L^{-1}.

Source: NAQUADAT 1985.

The term "total ammonia" refers to the sum of ionized and un-ionized forms (Butler 1964).

The concentration of ammonia (un-ionized) in aqueous systems is dependent primarily upon temperature, pH and total ammonia concentration, and, to a lesser extent, upon ionic strength and dissolved solids (Emerson *et al*. 1975). The concentration of un-ionized ammonia ($pK_a = 9.25$ at 25°C) increases with increasing pH and temperature. For example, un-ionized ammonia constitutes approximately 11% of total ammonia solutions at pH 8.5 and 20°C, but constitutes only 0.04% at pH 6.0 at the same temperature. Equations for calculating the fraction of total ammonia existing in the un-ionized form (i.e. ammonia) for pH 6-10 and 0-30°C and pH 5-12 and 0-40°C have been formulated (Thurston *et al*. 1979). The concentrations of un-ionized ammonia decrease as the ionic strength increases in hard water or dilute saline water. In most natural freshwater systems, the reduction in un-ionized ammonia concentrations attributable to dissolved solids (up to 200-300 mg·L^{-1}) is negligible (Emerson *et al*. 1975).

Ammonia in aqueous solutions may form complexes with a number of metal ions. It may also be sorbed onto suspended and bed sediments and to colloidal particles. Ammonia may also be exchanged between sediments and overlying water (Kemp and Mudrochova 1972).

The partial pressure of ammonia in solution increases with increasing pH, and, hence, substantial losses of ammonia via volatilization can occur. The loss of ammonia to the atmosphere increases with increasing wind speed, temperature and pH (Weiler 1979).

6.2.29.3.5 References

Brezonik, P.L. 1972. Nitrogen: sources and transformations in natural waters. *In* Nutrients in Natural Waters. H.E. Allen and J.R. Kramer (eds.). John Wiley & Sons, Toronto, Ontario. pp. 1-50.

Butler, J.N. 1964. Ionic Equilibrium. Addison-Wesley Publ. Co. Inc., Reading, Massachusetts. 547 pp.

CORPUS Information Services. 1984. Ammonium chloride. Ammonium nitrate. Ammonium phosphates. Ammonium sulfate. CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1985. Ammonia. CPI Product Profiles. Don Mills, Ontario.

Delwiche, C.C. 1973. The nitrogen cycle. *In* Chemistry in the Environment. C.L. Hamilton (ed.). W.H. Freeman and Co., San Francisco, California. pp. 42-52.

Emerson, K., R.C. Russo, R.E. Lund and R.V. Thurston. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. J. Fish. Res. Board Can. 32: 2379-2383.

Geadah, M.-L. 1985. National Inventory of Natural and Anthropogenic Sources and Emissions of Ammonia (1980). Environmental Protection Service, Environment Canada, Ottawa. EPS 5/IC/1.

Health and Welfare Canada. 1980. Ammonia. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 139-146.

Kemp, A.L.W. and A. Mudrochova. 1972. Distribution and forms of nitrogen in a Lake Ontario sediment core. Limnol. Oceanogr. 17: 855-867.

Klein, L. 1959. Chemical analysis. *In* River Pollution. Academic Press, New York. (Cited in Health and Welfare Canada 1980.)

Luebs, R.E., K.R. Davis and A.E. Laag. 1973. Ammonia and related gases emanating from a large dairy area. Calif. Agric. 27: 10-12. (Cited in Health and Welfare Canada 1980.)

Luebs, R.E., K.R. Davis and A.E. Laag. 1974. Diurnal fluctuation and movement of atmospheric ammonia and related gases from dairies. J. Environ. Qual. 3: 265-269.

Lund, H. 1971. Evolution of industrial pollution. *In* Industrial Pollution Control Handbook. H.B. Crawford and D.N. Fischel (eds.). McGraw-Hill Inc., New York. pp. 4-30. (Cited in Health and Welfare Canada 1980.)

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. Resources Agency of California State Water Resources Control Board. pp. 132-137.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Nitrogen – ammonia. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 26-27.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Pommen, L.W. 1983. The Effect on Water Quality of Explosives Use in Surface Mining. Vol. 1. Nitrogen Sources, Water Quality, and Prediction and Management of Impacts. British Columbia Ministry of Environment, Victoria, British Columbia. Tech. Rep. 4.

Robinson, E. and R.C. Robbins. 1968. Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants. Stanford Research Inst. Rep. No. N 71-25147, NTIS, U.S. Dep. of Commerce, Washington, D.C. 123 pp. (Cited in Health and Welfare Canada 198[illegible]

Thurston, R.V., R.C. Russo and K. Emerson. 1979. Aqueous Ammonia Equilibrium – Tabulation of Percent Un-ionized Ammonia. Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota. EPA Ecol. Res. Ser. EPA-600/3-79-091. 427 pp.

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. pp. 10-13.

Weiler, R.R. 1979. Rate of loss of ammonia from water to the atmosphere. J. Fish. Res. Board Can. 36: 685-689.

6.2.29.4 Nitrate

6.2.29.4.1 Uses and Production

Nitrates are used in the production of chemical fertilizers and as oxidizing agents in the chemical industry (McNeely *et al*. 1979; Health and Welfare Canada 1980). Ammonium nitrate, as well as sodium and calcium nitrate, are used in the production of explosives (Pommen 1983). The effectiveness of the waste stabilization process at sewage treatment plants is measured by the concentration of nitrates in the treated water (Ontario Ministry of the Environment 1981).

Canadian production and importation data for nitrate compounds appear in Table 6-36.

Table 6-36. Production and Importation of Nitrate Compounds in Canada

Compound	Amount (t)			
	Production		Importation	
	1981	1982	1981	1982
Potassium nitrate	1 643	1 606	2 669	2 445
Ammonium nitrate	70 809	74 635	10 937	10 365
Lead nitrate	—	—	97	273
Sodium nitrate	—	—	6 946	10 115
Calcium nitrate	—	—	6 903	6 543
Barium nitrate	—	—	46	11
Metallic nitrates	—	—	447	454
Silver nitrate	—	—	832	542

Sources: Statistics Canada 1983, 1984.

6.2.29.4.2 Sources and Pathways for Entering the Aquatic Environment

Most of the nitrogen used in biological reactions is of atmospheric origin, but loss of atmospheric nitrogen because of fixation by microorganisms is balanced by the release into the atmosphere of nitrogenous compounds from bacterial decomposition. Nitrogen is also fixed in the form of oxides by electrical discharges in the atmosphere and conveyed to the soil and water in the form of nitric and nitrous acids. These acids form nitrates and nitrites in the soil. There are five oxides of nitrogen in the atmosphere; the most abundant is nitrous oxide (N_2O) (Health and Welfare Canada 1980). Generally, nitrous oxide (N_2O) and nitric oxide (NO) are of biological origin (Fassett 1973). Some atmospheric ammonia may also be of biological origin, but its concentration is low. Nitrogen dioxide (NO_2), on the other hand, is generated by fossil fuel combustion (Health and Welfare Canada 1980).

Igneous rocks and volcanic emissions can contribute nitrates to water (McNeely *et al.* 1979). Some nitrate utilized by plants is returned to the soil, and some is lost in drainage and runoff (Health and Welfare Canada 1980). Upon complete oxidation, vegetable and animal debris and animal excrement can be significant natural sources of nitrates in water (McNeely *et al.* 1979).

Municipal and industrial wastewaters and septic tanks are the principal anthropogenic point sources of nitrates (U.S. EPA 1976). Explosives manufacturing and explosives use in mining and construction can also be significant sources of nitrate (Pommen 1983). Other sources include decomposition of sewage wastes, feedlot discharges and leachate from waste disposal dumps and sanitary landfills (U.S. EPA 1976; Ontario Ministry of the Environment 1981). Soil leaching in areas where inorganic nitrate fertilizers are used also contributes nitrates to river waters. Nitrate concentrations tend to be highest in the headwaters of these affected streams, especially during the spring and early summer months (Harmeson *et al.* 1971; Hill and McCague 1974; U.S. EPA 1976).

6.2.29.4.3 Environmental Concentrations

Surface waters contain at least trace levels of nitrates, but rarely as much as 5 mg·L^{-1} and often less than 1 mg·L^{-1} (McNeely *et al.* 1979; Ontario Ministry of the Environment 1981). Although some surface waters may contain more than 100 mg·L^{-1}, nitrate concentrations above 5 mg·L^{-1} may reflect unsanitary conditions, because one major source of nitrates is human and animal waste. Nitrate concentrations in surface waters may fluctuate, being somewhat higher in the winter months, when groundwater input is proportionately greater, and in the spring, when contributions from overland runoff are substantial (McNeely *et al.* 1979). Nitrate concentrations higher than several hundred micrograms per litre in lake surface waters tend to stimulate algal blooms and indicate eutrophic conditions (NAS 1978).

Concentrations of nitrates in groundwater may be high as a result of soil leaching (Ontario Ministry of the Environment 1981). In deep groundwater, nitrate concentrations may be considerable because of the absence of plants that utilize nitrates (Health and Welfare Canada 1980). In areas where inorganic nitrogen fertilizers are used, groundwaters may contain nitrate at concentrations of 1000 mg·L^{-1} (McNeely *et al.* 1979). The results of well testing in Ontario, Manitoba and Saskatchewan indicate generally low concentrations, with only about 13, 33 and 19% of the samples, respectively, having nitrate concentrations above 10 mg·L^{-1} (Robertson and Riddell 1949; Kay *et al.* 1953; Johnson 1955). Of drinking water supplies tested in Canada, 85% of the 123 stations sampled had nitrate and nitrite concentrations (as nitrogen) consistently lower than 1 mg·L^{-1} (NAQUADAT 1976). For more recent data on nitrate levels in Canadian surface waters, see Table 6-33 in Section 6.2.29.1.

Rainwater may contain a nitrate concentration of 0.2 mg·L^{-1} (McNeely *et al.* 1979). A 17-year study in Canada indicated that nitrate and nitrite accounted for 30-35% of the total nitrogen content of rain and snow, or about 290 mg·m^{-3} per year as nitrate (Fassett 1973).

6.2.29.4.4 Forms and Fate in the Aquatic Environment

The nitrate ion (NO_3^-) is the oxidized form of combined nitrogen found in natural waters. The nitrate salts of all common metals are soluble in water, resulting in neutral aqueous solutions. In dilute aqueous solutions, nitrate is chemically unreactive and has little tendency to form coordination complexes with metal ions (NAS 1978; McNeely *et al.* 1979).

Nitrate may be biochemically reduced to nitrite via denitrification. Such processes usually occur in anaerobic environments (Brezonik 1977).

6.2.29.4.5 References

Brezonik, P.L. 1977. Denitrification in natural waters. Prog. Water Technol. 8: 373-392.

Fassett, D.W. 1973. Nitrate and nitrites. *In* Toxicants Occurring Naturally in Foods. 2nd edition. Committee on Food Protection, National Academy of Sciences, U.S. National Research Council, Washington, D.C. (Cited in Health and Welfare Canada 1979.)

Harmeson, R.H., F.W. Sollo and T.E. Larson. 1971. The nitrate situation in Illinois. J. Am. Water Works Assoc. 63: 303-310.

Health and Welfare Canada. 1980. Nitrate. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 419-431.

Hill, A.R. and W.P. McCague. 1974. Nitrate concentrations in streams near Alliston, Ontario as influenced by nitrogen fertilization of adjacent fields. J. Soil Water Conserv. 29: 217-220.

Johnson, R.A. 1955. Incidence of nitrates in rural Ontario well waters. Can. J. Public Health 46: 30-34.

Kay, L.A., W.M. Ward and I.D. Hendin. 1953. Nitrates in Manitoba water supplies. Can. J. Public Health 44: 95-101.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Nitrogen. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 27-28.

NAQUADAT. 1976. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1978. Nitrates: An Environmental Assessment. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 723 pp.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Pommen, L.W. 1983. The Effect on Water Quality of Explosives Use in Surface Mining. Vol. 1. Nitrogen Sources, Water Quality, and Prediction and Management of Impacts. British Columbia Ministry of Environment, Victoria, British Columbia. Tech. Rep. 4.

Robertson, H.E. and W.A. Riddell. 1949. Cyanosis of infants produced by high nitrate concentration in rural waters of Saskatchewan. Can. J. Public Health 40: 72-77.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Industrial and Agricultural Chemical Products. Catalogue No. 46-224.

U.S. EPA. 1976. Nitrates, nitrites. *In* Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 107-110.

6.2.29.5 Nitrite

6.2.29.5.1 Uses and Production

Nitrite salts are used as corrosion inhibitors in industry. The presence of nitrites in water indicates active biological processes influenced by organic pollution (McNeely *et al.* 1979). Sodium and potassium nitrite may be added to meat binder, pickles and cured meat under the Food and Drugs Act (Health and Welfare Canada 1980).

In 1981 and 1982, 3734 and 2932 t, respectively, of sodium nitrite were imported into Canada. In the same year, 13 and 58 t, respectively, of metallic nitrites (metals not specified) were imported (Statistics Canada 1983).

6.2.29.5.2 Sources and Pathways for Entering the Aquatic Environment

Nitrites may be discharged by industries and municipal sewage plants (McNeely *et al.* 1979; Ontario Ministry of the Environment 1981). High nitrite concentrations are generally indicative of an industrial effluent (Ontario Ministry of the Environment 1981). Explosives manufacturing and explosives use in mining and construction can also be significant sources of nitrite (Pommen 1983). Nitrites may be formed in the rumen of animals and freshly cropped forage or moist feeds, because they are intermediate oxidation products of organic nitrogen (McNeely *et al.* 1979).

There is a minimal contribution of nitrites to the aquatic environment from atmospheric deposition (Health and Welfare Canada 1980). Amines and nitrates, which are readily converted to nitrite by microbial action, are present in the environment from both natural and man-made sources (U.S. EPA 1977). Because the nitrite ion is converted to the nitrate ion under oxidizing conditions, nitrite concentrations in the atmosphere will probably be quite low (Health and Welfare Canada 1980).

Table 6-37. Environmental Concentration Ranges for Nitrite in Canadian Surface Waters

Region	Concentration range ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<0.002[1]-0.01	49	1980
Western	0[1]-0.1216	50	Prior to 1980
Central	0[1]-25	2573	Prior to 1980
Atlantic	0.005[1]-0.0714	38	Prior to 1980
	<0.005[2]	26	1980

[1] Detection limit is not stated (dissolved).

[2] Detection limit is not stated (total).

Source: NAQUADAT 1985.

6.2.29.5.3 Environmental Concentrations

The nitrite ion is less stable than the nitrate ion. Because nitrites are rapidly oxidized to nitrates, they are seldom present in surface waters in significant concentrations (Health and Welfare Canada 1980). Nitrite concentrations seldom exceed 1.0 $mg \cdot L^{-1}$ as nitrogen (McNeely *et al.* 1979; Ontario Ministry of the Environment 1981). Usually nitrite concentrations are in the order of 1 $\mu g \cdot L^{-1}$ (McNeely *et al.* 1979). Nitrites may be found in groundwater (NAQUADAT 1985).

Available data indicate that nitrite levels in rain and snow are 1-5% of nitrate concentrations (Fassett 1973).

Environmental concentration ranges for nitrite in Canadian surface waters are presented in Table 6-37.

6.2.29.5.4 Forms and Fate in the Aquatic Environment

The nitrite ion (NO_2^-) contains nitrogen in an intermediate and relatively unstable oxidation state (+3). Nitrite salts are soluble, although they are not as common as nitrate salts. Nitrite may also form strong complexes with many transition metals; however, because of the usually low concentrations of nitrite in natural waters, such complexes are probably not environmentally significant (NAS 1978).

The nitrite ion is the conjugate base of nitrous acid (pK_a 3.36), and, in most waters, the acid readily dissociates. Nitrite is a weak reducing agent and may be oxidized to nitrate (NAS 1978).

Nitrite is produced biochemically by incomplete nitrification of ammonia and by denitrification of nitrate. It is usually present only under conditions of limited oxygen supply (Bezonik 1972; Wetzel 1975).

Nitrosamines may be formed from nitrite *in vivo* in animals (U.S. EPA 1977; NAS 1978).

6.2.29.5.5 References

Bezonik, P.L. 1972. Nitrogen: sources and transformations in natural waters. *In* Nutrients in Natural Waters. H.E. Allen and J.R. Kramer (eds.). John Wiley & Sons, Toronto, Ontario. pp. 1-50.

Fassett, D.W. 1973. Nitrates and nitrites. *In* Toxicants Occurring Naturally in Foods. 2nd edition. Committee on Food Protection, National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Health and Welfare Canada. 1980. Nitrite. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 451-455.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Nitrogen. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 28.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1978. Nitrates: an Environmental Assessment. U.S. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 723 pp.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Pommen, L.W. 1983. The Effect on Water Quality of Explosives Use in Surface Mining. Vol. 1. Nitrogen Sources, Water Quality, and Prediction and Management of Impacts. British Columbia Ministry of Environment, Victoria, British Columbia. Tech. Rep. 4.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1977. Scientific and Technical Assessment Report on Nitrosamines. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA-600/6-77-001.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.30 Oxygen (Dissolved)

6.2.30.1 Introduction

An adequate supply of dissolved oxygen is essential for the maintenance of self-purification processes in natural water systems and waste treatment plants. By measuring the dissolved oxygen content, the effects of oxidizable wastes on receiving waters and the efficiency of waste treatment during biochemical oxidation may be assessed. Dissolved oxygen levels also indicate the capacity of a natural body of water for maintaining aquatic life (Wetzel 1975).

6.2.30.2 Sources and Pathways for Entering the Aquatic Environment

The oxygen dissolved in water may be derived either from the atmosphere or from photosynthesis by aquatic plants, including phytoplankton. Roughly 35% of the amount of oxygen dissolved in water is from the atmosphere. Biological depletion and re-aeration processes control dissolved oxygen concentrations. The decomposition of organic matter and oxidation of inorganic wastes may reduce dissolved oxygen levels, sometimes leading to potentially anaerobic conditions (Wetzel 1975).

6.2.30.3 Environmental Concentrations

The concentration of dissolved oxygen in natural surface water is usually less than 10 mg·L^{-1} (McNeely *et al.* 1979). In British Columbia, dissolved oxygen concentrations are typically greater than 10 mg·L^{-1}, i.e. near saturation at temperatures which occur below the range of 7-15°C (Buchanan 1985).

Environmental concentration ranges for dissolved oxygen in Canadian surface waters are presented in Table 6-38.

Table 6-38. Environmental Concentration Ranges for Dissolved Oxygen in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.1[1]-16.2	4531	Prior to 1980
Western	ND[1,2]-18.4	2409	1980-1985
Central	ND[1]-17.55	2404	1980-1985
	3[3]-140	716	Prior to 1980
Atlantic	2.2[1]-16.8	1774	1980-1985
	1[3]-124	242	Prior to 1980

[1] Detection limit is 0.01 mg·L^{-1} (dissolved).

[2] ND = not detected.

[3] % saturation; calculated values from dissolved oxygen concentration at the temperature of sampling.

Source: NAQUADAT 1985.

Large variations in dissolved oxygen exist seasonally and geographically. These variations are in part a result of variations in temperature, photosynthetic activity and river discharge, and may be observed on a large or small time scale (Tarzwell and Gaufin 1953).

6.2.30.4 Forms and Fate in the Aquatic Environment

Oxygen is a fundamental constituent of natural waters. It is moderately soluble in water. The amount of dissolved oxygen in natural water varies with temperature, salinity, turbulence (mixing) of the water and atmospheric pressure (decreasing with altitude). The solubility of atmospheric oxygen (i.e. saturation) in fresh water ranges from approximately 15 mg·L^{-1} at 0°C to 8 mg·L^{-1} at 25°C and at sea level. Seawater saturation ranges from 11 mg·L^{-1} at 0°C to 7 mg·L^{-1} at 25°C (McNeely *et al.* 1979). The oxygen content of water decreases as temperature and salinity increase. There is about 20% less dissolved oxygen in normal seawater than in fresh water (Wetzel 1975; Davis 1975). Horizontal stratification of dissolved oxygen in lakes may be related to pockets of photosynthesis or respiration and the decay of organic material (Wetzel 1975; Davis 1975; Alabaster and Lloyd 1982).

Bacterial respiration during the decomposition of sedimenting organic matter is the major cause of oxygen depletion, and is most intense at the sediment-water interface. Lake depth is a major factor in dissolved oxygen levels in the hypolimnetic layer. Plant and animal respiration also consume large amounts of dissolved oxygen. In addition, the chemical oxidation of dissolved organic matter and nutrient discharges from natural or man-made sources results in oxygen depletion (Wetzel 1975; Davis 1975).

6.2.30.5 References

Alabaster, J.S. and R. Lloyd. 1982. Dissolved oxygen. *In* Water Quality Criteria for Freshwater Fish. 2nd edition. Butterworth Scientific, London. pp. 127-142.

Buchanan, R.J. 1985. Personal communication. Water Management Branch, British Columbia Ministry of Environment, Victoria, British Columbia.

Davis, J.C. 1975. Waterborne Dissolved Oxygen Requirements and Criteria with Particular Emphasis on the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14100. 111 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Dissolved oxygen. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 33-34.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Tarzwell, C.M. and A.R. Gaufin. 1953. Some important biological effects of pollution often disregarded in stream surveys. *In* Proc. 8th Ind. Waste Conf. Purdue Univ. Eng. Bull. Ser. 83: 295-316. (Cited in Davis 1975.)

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.31 Phosphorus

6.2.31.1 Uses and Production

In Canada, approximately 75% of phosphate rock is used in fertilizer production, 18% in elemental phosphorus production and 6% in calcium phosphate production. Other uses for phosphorus include organic and inorganic chemicals, soaps and detergents, pesticides, insecticides, alloys, animal food supplements, motor lubricants, ceramics, beverages, catalysts, photographic materials and dental and silicate cements (Barry 1985). Polyphosphates are used as scale and corrosion inhibitors in some public water supplies and industrial boiler systems (Ontario Ministry of the Environment 1981).

Sedimentary phosphate rock, or phosphorite, is the most widely used phosphate raw material. Apatite, which is second in importance, occurs in many igneous and metamorphic rocks. Known Canadian deposits are limited and currently not economically recoverable. They occur as apatite deposits in Ontario and Quebec, and as sedimentary phosphate rock deposits in the Rocky Mountains (Barry 1985).

World phosphate rock production in 1983 and 1984 was estimated at 130.8×10^6 and 143×10^6 t, respectively. World exports of phosphate rock in 1983 and 1984 were 46.4×10^6 and 48×10^6 t, respectively (Barry 1985).

Canadian phosphate fertilizer shipments to domestic markets for 1982/83 and 1983/84 were 548 381 and 600 161 t, respectively. Canadian phosphate fertilizer shipments to export markets for 1982/83 and 1983/84 were 631 574 and 670 603 t, respectively. Phosphorus is currently produced in Quebec and Newfoundland (CORPUS Information Services 1985). Production of phosphorus and consumption, importation and exportation of phosphorus and phosphate compounds in Canada are presented in Table 6-39.

6.2.31.2 Sources and Pathways for Entering the Aquatic Environment

Phosphorus may be removed from igneous and other types of rock by leaching or weathering (Wetzel 1975). The minerals fluorapatite ($Ca_5(PO_4)_3F$), hydroxylapatite ($Ca_5(PO_4)_3OH$), strengite ($Fe(PO_4)\cdot 2H_2O$), whitlockite ($Ca_3(PO_4)_2$) and berlinite ($AlPO_4$) may release phosphorus to surface waters (Faust and Aly 1981). The decomposition of organic matter is another source of phosphorus (IJC 1980; Ontario Ministry of the Environment 1981).

Domestic effluents, industrial effluents and agricultural drainage from fertilized land contribute phosphorus to waters. Phosphates may be added to water supplies to prevent scale formation, inhibit corrosion and enhance laundry and cleaning efficiency (McNeely *et al.* 1979). Atmospheric deposition and soil erosion also contribute phosphorus to the aquatic environment (Wetzel 1975).

6.2.31.3 Environmental Concentrations

Phosphorus is rarely found in high concentrations in surface water, because it is actively taken up by plants. It has been well established that phosphorus is the nutrient that commonly limits freshwater phytoplankton communities (IJC 1980). Phosphate concentrations between 0.01 and 0.05 $mg \cdot L^{-1}$ are generally found in most natural surface waters, although concentrations range from below 0.001 $mg \cdot L^{-1}$ in natural waters to above 200 $mg \cdot L^{-1}$ in closed saline lakes (Wetzel 1975). Environmental concentration ranges for phosphorus and phosphate in Canadian surface waters are presented in Table 6-40. There is a large spatial and temporal variation in concentrations. Generally, elevated phosphorus concentrations are found in lakes with drainage from sedimentary areas rich in phosphatic rock and lakes rich in organic matter. Lower concentrations of phosphorus in natural waters are common in mountainous regions with a crystalline geomorphology.

Groundwater phosphorus concentrations average approximately 0.02 $mg \cdot L^{-1}$. The phosphorus content of precipitation is generally less than 0.03 $mg \cdot L^{-1}$ in background areas, but may increase to more than 0.1 $mg \cdot L^{-1}$ in urban and industrial areas (Wetzel 1975).

6.2.31.4 Forms and Fate in the Aquatic Environment

Phosphorus, a nonmetallic element having oxidation states of +1, +3 and +5, can occur in numerous organic and inorganic forms, and can be present in waters as dissolved and particulate species. Elemental phosphorus does not often occur in the natural environment; instead, orthophosphates, pyrophosphates, metaphosphates, polyphosphates and organically bound phosphates are found in natural waters and wastewaters. In water, the form of the element is continually changing because of processes of decomposition and synthesis between organically bound forms and oxidized inorganic forms. The principal dissolved phosphate species in water between pH 5 and 9 are $H_2PO_4^-$ and HPO_4^{2-}. Major pyrophosphate species at neutral pH are $H_2P_2O_7^{2-}$ and $HP_2O_7^{3-}$ (Hutchinson 1957; Wetzel 1975; Pierrou 1979; NAQUADAT 1985).

Phosphorus associated with particulate matter in the aquatic environment can be found in organisms, in mineral phases of rocks and soil and adsorbed onto particulate organic matter or onto macro-organic aggregations. Dissolved inorganic phosphorus, in addition to the inorganic species mentioned above, includes orthophosphate (PO_4^{3-}), polyphosphates and organic colloids or phosphorus combined with adsorptive colloids (Hutchinson 1957; Wetzel 1975; Stumm and Morgan 1981).

The phosphorus cycle in natural waters has been extensively studied (Hutchinson 1957; Wetzel 1975; Pierrou 1979). It is influenced by the exchange of phosphorus between sedimentary and aqueous compartments. This exchange is influenced by several physical-chemical and biological modifying

Table 6-39. Production of Phosphorus and Consumption, Importation and Exportation of Phosphorus and Phosphate Compounds in Canada

Parameter	Compound	Amount (t)		
		1982	1983	1984
Production	Phosphorus	60 000	61 000	68 000
Consumption	Phosphorus	[illegible]9 600	20 600	21 000
	Phosphate rock	2 3[illegible] 671	2 830 000	3 029 000
Importation	Phosphorus	1 800	1 400	1 600
	Phosphate rock	2 511 724	2 662 725	2 593 566
	Calcium phosphate	18 268	33 179	30 847
	Normal superphosphate fertilizers ($\leq$22% P_2O_5)	188	1 368	18
	Triple superphosphate fertilizers ($>$22% P_2O_5)	31 947	54 755	30 804
	Phosphate fertilizers (group not specified)	217 693	304 181	198 551
	Potassium phosphates	1 492	1 729	1 503
	Sodium phosphate, tribasic	636	1 013	662
Exportation	Phosphorus	42 000	42 000	48 600
	Nitrogen phosphate fertilizers (group not specified)	272 086	202 514	168 059

Sources: Barry 1985; CORPUS Information Services 1985.

factors, including mineral-water equilibria, sorption, redox interactions and the activities of bacteria, fungi, plankton and invertebrates (Hutchinson 1957; Wetzel 1975).

Phosphorus in sediments occurs predominantly as apatite, nonapatite inorganic phosphorus, organic phosphorus and orthophosphate associated with hydrated ferric oxides. Under aerobic conditions, phosphorus is associated primarily with the sedimentary phase. Under anaerobic conditions, reduction of ferric hydroxides and ferric complexes occurs with the release of ferrous iron and phosphorus into the overlying water. Phosphorus may also be mobilized by numerous bacteria, especially of the genera *Pseudomonas*, *Bacterium* and *Chromobacterium*, which are abundant in sediments. The rate of release of phosphorus from sediments is also increased by agitation resulting from turbulence (Wetzel 1975).

Phosphorus is considered to be an essential macronutrient, and is readily accumulated by a variety of living organisms (Wetzel 1975; Pierrou 1979; Bowen 1979). Elevated concentrations of phosphorus in some water bodies contribute to accelerated eutrophication (Wetzel 1975). Concentrations of phosphorus range from 2800 to 4000 in marine algae and average 18 000 mg·kg^{-1} in fish. Concentrations average 0.06 and 0.02 mg·L^{-1} in fresh and marine waters, respectively (Bowen 1979).

6.2.31.5 References

Barry, G.S. 1985. Phosphate. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 45.1-45.17.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

CORPUS Information Services. 1985. Phosphorus (white, red and black element P_4). CPI Product Profile. Don Mills, Ontario.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, New York. 1015 pp.

IJC. 1980. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Phosphorus. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 46-47.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Pierrou, U. 1979. The phosphorus cycle: quantitative aspects and the role of man. *In* Biogeochemical Cycling of Mineral-forming Elements. P.A. Trudinger and D.J. Swaine (eds.). Elsevier Scientific Publ. Co., Amsterdam. pp. 205-210.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, New York. 780 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

Table 6-40. Environmental Concentration Ranges for Phosphorus and Phosphate in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	$<0.005^{1}$-0.032	3	Prior to 1980
	0.0013^{2}-1.76	854	1980-1985
Western	0.003^{3}-3.0	7324	1980-1985
	0.019^{1}-0.49	29	1980-1985
	0.003^{2}-3.0	7103	1980-1985
Central	$ND^{3,4}$-0.6	112	Prior to 1980
	0.001^{1}-0.21	613	1980-1985
	ND^{2}-12.84	3413	1980-1985
Atlantic	0.001^{3}-0.037	87	1980-1985
	0.33^{1}-0.4	2	Prior to 1980
	0.001^{2}-4.3	4994	1980-1985

[1] Detection limit is 0.003 mg·L^{-1} (total inorganic phosphorus).
[2] Detection limit is 0.002 mg·L^{-1} (total phosphorus).
[3] Detection limit is 0.001 mg·L^{-1} (total phosphate).
[4] ND = not detected.

Source: NAQUADAT 1985.

6.2.32 Potassium

6.2.32.1 Uses and Production

Potassium compounds are extensively utilized in the production of fertilizers; about 95% of all potassium chloride production is for this purpose. Potassium chloride and its derivatives, potassium nitrate, potassium carbonate, potassium hydroxide and potassium chlorate, are also used in the manufacturing of matches, vat dyes, glassware, china, pharmaceuticals, synthetic rubber, soaps and detergents, photographic films, curing agents for meats, fumigants and insecticides (NRCC 1977).

In Canada, potassium chloride production occurs almost exclusively in the province of Saskatchewan, with nominal production occurring in New Brunswick. The refined ore (KCl) is referred to as potassium chloride, muriate of potash or potash (NRCC 1977). World production of potash was 28 547 t in 1984. Canada is the second largest potash producer, with 27% of world production, slightly behind the U.S.S.R. production of 31.5% (Barry 1985).

Production, consumption, importation and exportation figures of potassium chloride, potassium hydroxide and potassium sulphate in Canada are presented in Table 6-41.

Table 6-41. Production, Consumption, Importation and Exportation of Potassium Chloride, Potassium Hydroxide and Potassium Sulphate in Canada

		Amount (t)		
Parameter	Compound	1982	1983	1984
Production	Potassium chloride (K_2O equivalent)	5 351 786	5 929 567	7 500 000
	Potassium hydroxide (caustic potash)	6 100	6 700	7 500
	Potassium sulphate[1]	—	—	—
Consumption	Potassium chloride	380 500	384 300	435 800
	Potassium hydroxide	7 900	8 200	8 800
	Potassium sulphate	71 500	65 300	62 800
Importation	Potassium chloride	1 881	2 277	1 609
	Potassium sulphate	77 000	62 300	60 800
	Potassic fertilizer (group not specified)	57 650	47 367	7 650
	Potassium carbonate	1 113	1 555	1 529
	Potassium hydroxide	3 407	2 936	1 811
	Potassium nitrate	2 444	4 343	2 653
	Potassium phosphate	1 492	1 729	1 503
	Potassium silicates	686	813	535
Exportation	Potassium chloride	7 221 493	8 963 834	8 214 829
	Potassium hydroxide[2]	—	—	—
	Potassium sulphate[2]	—	—	—

[1] Production of potassium sulphate is scheduled to begin in mid-1985 when a projected 4000 t are to be produced.

[2] No exports.

Sources: Barry 1985; CORPUS Information Services 1985.

6.2.32.2 Sources and Pathways for Entering the Aquatic Environment

Although potassium may be found in many rocks, those with significant amounts of potassium (e.g. granite) are resistant to weathering. Evaporitic rocks containing large amounts of potassium do not occur frequently. Feldspar, feldspathoids, micas and clay minerals all contain appreciable amounts of potassium and, thus, are potential natural sources of potassium in water. Since potassium salts are widely used in industry and, particularly, agriculture, they can be introduced into the aquatic environment by industrial effluents and from leaching of potassium-bearing soils. There are no data available to indicate the contribution of potassium chloride to the environment from its use as a fertilizer (NRCC 1977; Bowen 1979).

6.2.32.3 Environmental Concentrations

Although potassium constitutes about 2.5% of the earth's crust and is one of the principal alkali metals present in water, it is found in quantities of only a few milligrams per litre in water (McNeely *et al.* 1979).

The concentration of potassium in natural surface water seldom reaches 20 $mg\cdot L^{-1}$ and is generally less than 10 $mg\cdot L^{-1}$. Environmental concentration ranges for potassium in Canadian surface waters are presented in Table 6-42. The sodium-potassium ratio in natural waters ranges from 2:1 to 3:1, with the proportion of sodium increasing with increasing sodium plus potassium concentration. Potassium concentrations as high as 100 $mg\cdot L^{-1}$ occur in hot springs, whereas brines may contain up to 25 000 $mg\cdot L^{-1}$ (McNeely *et al.* 1979).

Table 6-42. Environmental Concentration Ranges for Potassium in Canadian Surface Waters

Region	Concentration range ($mg\cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[1,2]-9.3	1465	1980-1985
Western	0.03[2]-33.0	2930	1980-1985
Central	ND[2]-7	3636	1980-1985
Atlantic	0.26[3]-1.52	7	Prior to 1980
	0.01-32.0	9212	1980-1985

[1] ND = not detected.

[2] Detection limit is 0.1 $mg\cdot L^{-1}$ (dissolved).

[3] Detection limit is 0.2 $mg\cdot L^{-1}$ (total).

Source: NAQUADAT 1985.

The total content of potassium in most soils is about 1-2%, which is lower than the average potassium content of igneous rocks, but higher than that of some sedimentary rocks. A small proportion of potassium is exchangeable and is present as soluble salts (NRCC 1977).

6.2.32.4 Forms and Fate in the Aquatic Environment

Potassium is found predominantly in ionic form in water. Potassium salts are readily soluble in water and are seldom hydrated. The aqueous ion undergoes few significant precipitation reactions, and is only weakly complexed by simple anions and not at all by monodentate neutral ligands. It does, however, enter into ion exchange reactions (Cotton and Wilkinson 1980; Faust and Aly 1981). The natural leaching of potassium from minerals does not result in significantly increased solubilization (sodium, on the other hand, remains in solution). Instead, potassium is usually readily incorporated into new mineral structures (McNeely *et al.* 1979). For example, the clay mineral vermiculite has a special affinity for the potassium ion, whereby the ion is initially adsorbed and then efficiently trapped in the layered structure of the mineral ("potassium fixation") and removed from direct interaction with the surrounding media (NAS 1977).

Potassium is essential for plant and animal nutrition, and therefore is readily accumulated. Average concentrations of potassium in fresh and salt water are 2.2 and 399 mg·L^{-1}, respectively. In comparison, potassium levels in various organisms are significantly higher (e.g. terrestrial vegetation, 5000-34 000 mg·kg^{-1}; edible vegetables, 1000-68 000 mg·kg^{-1}; marine algae, 32 000-52 000 mg·kg^{-1}; marine fish, 15 000 mg·kg^{-1}; mammalian bone, 2100 mg·kg^{-1}; mammalian muscle, 16 000 mg·kg^{-1}) (Bowen 1979).

6.2.32.5 References

Barry, G.S. 1985. Potash. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 47.1-47.15.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

CORPUS Information Services. 1985. Potash (potassium chloride; muriate). Potassium hydroxide (caustic potash). Potassium sulfate (including sulfate of potash magnesia). CPI Product Profiles. Don Mills, Ontario.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Potassium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p.48.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Committee on Safe Drinking Water. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

NRCC. 1977. The Effects of Alkali Halides in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15019. 171 pp.

6.2.33 Selenium

6.2.33.1 Uses and Production

Selenium is used in a wide variety of manufacturing industries, including electronic, metallurgic, glass and ceramic, pigment, chemical and pharmaceutical industries. In Canada, selenium is mainly used in glass manufacturing (73%) (Wood 1975; Demayo, Taylor *et al.* 1979). Examples of uses of selenium are presented in Table 6-43.

The concentration of selenium in minerals is too low to make its extraction economically feasible (Health and Welfare Canada 1980). Most selenium for industrial and commercial purposes is produced from electrolytic copper-refining slimes and from flue dusts from copper and lead smelters. Selenium production, therefore, is related to refined copper production and to the relative recovery rates of selenium (Cranstone 1984). The world's major selenium producers are Canada, the United States and Japan. In 1981, the production of selenium in all forms from Canadian refineries was 350 t, and domestic consumption was 9.4 t. Canada exports most of its product to the United States (163.2 t in 1981) and Great Britain (64.6 t in 1981) (Cranstone 1984). In 1984, 354 t of selenium were produced in Canada; the major producing provinces were Ontario (224 t), Manitoba (68 t) and Quebec (51 t) (Energy, Mines and Resources Canada 1985).

Table 6-43. Uses of Some Inorganic Selenium Compounds

Compound	Uses
Aluminum selenide, Al_2Se_3	Preparation of hydrogen selenide; semiconductors
Ammonium selenite, $(NH_4)_2SeO_3$	Manufacture of red glass; reagent for alkaloids
Arsenic hemiselenide, As_2Se	Manufacture of glass
Bismuth selenide, Bi_2Se_3	Semiconductors
Cadmium selenide, CdSe	Photoconductors, semiconductors, photoelectric cells and rectifiers; phosphors
Calcium selenide, CaSe	Electron emitters
Cupric selenate, $CuSeO_4$	Colouring Cu or Cu alloys black
Cupric selenide, CuSe	Catalyst in Kjeldahl digestions; semiconductors
Indium selenide, InSe	Semiconductors
Potassium selenate, K_2SeO_4	Reagent
Selenium disulphide, SeS_2	Remedies for eczemas and fungus infections in dogs and cats; antidandruff agent in shampoos for human use; usually employed as a mixture with the monosulphide
Selenium hexafluoride, SeF_6	Gaseous electric insulator
Selenium monosulphide, SeS	Topically against eczemas, fungal infections, demodectic mange, fleabites in small animals; usually employed as a mixture with the disulphide
Selenium dioxide, SeO_2	Manufacture of other selenium compounds; reagent for alkaloids
Sodium selenate, Na_2SeO_4	Veterinary therapeutic agent
Sodium selenite, Na_2SeO_3	Removing green colour from glass during its manufacture; veterinary therapeutic agent

Source: NAS 1976.

6.2.33.2 Sources and Pathways for Entering the Aquatic Environment

Selenium is widely distributed in the earth's crust at concentrations averaging 0.09 mg·kg^{-1} (Stahl 1969). It occurs naturally in waters in trace amounts as a result of geochemical processes such as weathering of rocks and erosion of soils (Health and Welfare Canada 1980), or as a result of volcanic activity (NAS 1976; Marier and Jaworski 1983). An estimated 7200 t of selenium enter the global environment annually by weathering (Bertine and Goldberg 1971). Another study estimates that the dissolved selenium in the world's river water contributes about 80%, and the suspended sediment, 20%, to the amount of dissolved selenium in the oceans (Kharkar *et al.* 1968). Little information is available on the amount of selenium entering the global environment by volcanic activity (Demayo, Taylor *et al.* 1979).

Volcanic activity is regarded as the main source of selenium in seleniferous regions (Lakin and Davidson 1967; NAS 1976; Wilber 1980: Marier and Jaworski 1983). Selenium is frequently found in significant amounts in deposits of native sulphur and sulphide ores of heavy metals (Luttrell 1959; Davidson 1960; U.S. EPA 1980); it is also found in coal (0.1-5 $\mu g \cdot g^{-1}$) (Demayo, Brien *et al.* 1979) and oil (<6-2200 $\mu g \cdot L^{-1}$) (NAS 1976; Demayo, Taylor *et al.* 1979).

Although the major source of selenium in the environment is the weathering of rocks and soils (Rosenfeld and Beath 1964), worldwide human activities contribute about 3500 $t \cdot a^{-1}$ (U.S. EPA 1975). Studies indicate that selenium concentrations are lowest in water bodies geographically isolated from large urban centres (Traversy *et al.* 1975). Anthropogenic sources of selenium in water bodies include effluents from copper and lead refineries and probably municipal sewage (NAS 1976; Demayo, Taylor *et al.* 1979; Health and Welfare Canada 1980; IJC 1981).

There is some indication that atmospheric emissions from burning fossil fuels may contribute selenium to natural waters (Copeland 1970; Traversy *et al.* 1975; Health and Welfare Canada 1980). Emissions of selenium to the atmosphere from industrial sources have been small (360 t) (NAS 1976). In 1970, the burning of coal was estimated to account for 62% of the total industrial selenium emissions worldwide, and mining-smelting-refining operations accounted for 26%. The burning of oil and industrial processes that utilize selenium account for the remaining emissions (U.S. EPA 1972; NAS 1976; Marier and Jaworski 1983). One review estimated that the total annual selenium emissions from global human activities (coal and oil burning and industrial sources) are about 5400 t (Demayo, Taylor *et al.* 1979).

The most recent information available on emissions to the Canadian environment was reported for 1973. In that year, total Canadian selenium emissions to the atmosphere were estimated at 179.2 t. The primary copper and nickel industry was the largest emissions contributor at 89.7 t, or 50.2% of the total. The combustion of coal accounted for 24.9%, or 46.6 t, and selenium processing (copper refineries) accounted for an additional 18.5%, or 33.1 t. Ontario accounted for 55% of total Canadian selenium emissions to the atmosphere (Nadon and Sheffield 1977).

6.2.33.3 Environmental Concentrations

The concentration of selenium in Great Lakes waters ranges from 0.01 to 5.0 $\mu g \cdot L^{-1}$ (Hodson *et al.* 1983), whereas the average concentration for rivers of the Great Lakes basin is 0.1 $\mu g \cdot L^{-1}$ with an upper limit of 0.5 $\mu g \cdot L^{-1}$ (Traversy *et al.* 1975). Seawater contains 0.09 ± 0.03 $\mu g \cdot L^{-1}$ selenium (Lakin and Davidson 1967). The higher selenium content of some fresh waters compared with that of seawater is probably a result of the more intimate contact between fresh water and selenium-rich rocks and soils (Marier and Jaworski 1983). The average selenium concentration of rainwater and snowmelt in the Great Lakes basin ranges from less than 0.1 to 0.8 $\mu g \cdot L^{-1}$ (Traversy *et al.* 1975). Although waters seeping from seleniferous deposits may result in selenium concentrations as high as 400 $\mu g \cdot L^{-1}$, surface waters in most areas contain less than 1.0 $\mu g \cdot L^{-1}$ (Lakin and Davidson 1967). Sediment concentrations in the Great Lakes are normally less than 1 $\mu g \cdot g^{-1}$ (dry weight) (IJC 1981). Environmental concentration ranges for selenium in Canadian surface waters are presented in Table 6-44.

Table 6-44. Environmental Concentration Ranges for Selenium in Canadian Surface Waters

Region	Concentration range[1] ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	0.1-0.2	19	Prior to 1980
Central	0.1-4	139	1980-1981
Atlantic	<0.5-1	35	1980

[1] Detection limit is 0.1 $\mu g \cdot L^{-1}$.

Source: NAQUADAT 1985.

Table 6-45. Selenium Concentrations in Tissues of Organisms Sampled from the Great Lakes

Organism/tissue	Year	Concentration ($\mu g \cdot g^{-1}$)
Phytoplankton	1980	0.76 – 3.4 (dry weight)
Zooplankton	1973, 1980	1.6 – 4.8 (dry weight)
Fish (14 species)	1973, 1974, 1980	100 – 1550 (wet weight)
Herring gull	1977	
eggs (33 samples)		<0.4 – 1.3 (wet weight)
adult liver (17 samples)		0.31 ± 0.114[1] (wet weight)
adult feathers (17 samples)		2.60 ± 1.22[1] (wet weight)

[1] Standard deviation.

Source: IJC 1981.

Data for selenium concentrations in Canadian drinking water are limited to a 1975 study in Manitoba. One hundred and twelve of 120 stations had concentrations below 5 $\mu g \cdot L^{-1}$, and no station exceeded 10 $\mu g \cdot L^{-1}$ selenium (Health and Welfare Canada 1980). The ranges for selenium concentrations in tissues of various organisms sampled from the Great Lakes are summarized in Table 6-45. Almost all of a number of fish species, representing 438 specimens, taken from New York State waters contained less than 1 $\mu g \cdot g^{-1}$ (wet weight) selenium (Pakkala *et al.* 1972).

6.2.33.4 Forms and Fate in the Aquatic Environment

The chemical behaviour of selenium resembles that of sulphur and tellurium (U.S. EPA 1979). Selenium exists in the natural environment in four oxidation states: 0; −2, selenide ion (Se(II)); +4, selenite oxyanion (SeO_3^{2-}); and +6, selenate oxyanion (SeO_4^{2-}) (U.S. EPA 1979, 1980; Health and Welfare Canada 1980; Shamberger 1981). The oxidation state of selenium results in different chemical properties that affect its movement in the aquatic environment (U.S. EPA 1979). Inorganic and organic selenides either are insoluble or rapidly decompose, under aerobic conditions, to form elemental selenium, which is insoluble in water (U.S. EPA 1979, 1980). This form of the element is considered to be inert, and appears to be a major sink for selenium in the aquatic environment (U.S. EPA 1979, 1980). Dissolved selenium species in the aquatic environment are predominantly in the form of selenites and selenates (U.S. EPA 1979, 1980; Health and Welfare Canada

1980). Any dissolved selenite would be present primarily as the biselenite ion in water of pH 3.5-9.0 (U.S. EPA 1979). Selenites have an affinity for iron and aluminum sesquioxides, forming stable complexes (U.S. EPA 1980). Most selenites are less water-soluble than are selenates; in particular, ferric selenites are insoluble, thereby effectively removing selenites from the water column (U.S. EPA 1979). Under acidic and reducing conditions, selenites are reduced to elemental selenium, which is then removed from the water column (NAS 1976; U.S. EPA 1980). Alkaline and oxidizing conditions favour the formation and stability of the selenates, which are not highly complexed by sesquioxides, are soluble and are readily available for uptake by aquatic organisms (NAS 1976; U.S. EPA 1979, 1980).

The half-life of selenium in fresh water prior to precipitation to the sediments is 25-50 d (IJC 1981). Precipitation of selenium, however, evidently requires contact with suspended and bed solids, although sediment type does not seem to influence its disappearance from the water column (Rudd *et al.* 1980).

Selenium can be methylated by a variety of organisms, including benthic microflora (Stadtman 1974; Chau *et al.* 1976). Dimethyl selenide and dimethyl diselenide are produced, and may volatilize, thereby removing selenium from the water column (U.S. EPA 1979).

Selenium is found in trace quantities in most plant and animal tissues (Underwood 1971), and is essential to some plants and microbes and to all vertebrates (Bowen 1979). Very few quantitative data are available on the bioaccumulation of selenium in aquatic organisms. Concentration factors of 800 have been reported for freshwater plants (Chapman *et al.* 1968), and 8-400 for freshwater invertebrates and fish (Chapman *et al.* 1968; Hodson *et al.* 1980). Selenium appears to be slowly eliminated. For example, selenium in carp (*Cyprinus carpio* L.) had a biological half-life of about 28 d (Sato *et al.* 1980). With respect to both bioconcentration and toxicity, dietary selenium, rather than waterborne selenium, seems to be the most important source of the element in many freshwater organisms; however, little biomagnification occurs (Sandholm *et al.* 1973; U.S. EPA 1980; Hilton *et al.* 1980).

6.2.33.5 References

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, New York. 333 pp.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. (Cited in U.S. EPA 1980.)

Chau, Y.K., P.T.S. Wong, B.A. Silverberg, P.L. Luxon and G.A. Bengert. 1976. Methylation of selenium in the aquatic environment. Science 192: 1130-1131.

Copeland, R. 1970. Selenium: the unknown pollutant. Limnos 3: 7-9.

Cranstone, D.A. 1984. Selenium and tellurium. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

Davidson, D.F. 1960. Selenium in Some Epithermal Deposits of Antimony, Mercury, and Silver and Gold. U.S. Geol. Surv. Bull. No. 1112-A. U.S. Government Printing Office, Washington, D.C.

Demayo, A., M.C. Taylor and S.W. Reeder. 1979. Selenium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Demayo, A., E. Brien and K.W. Taylor. 1979. Elemental Composition of Fossil Fuels and Their Ashes. A Review. Unpublished report. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Energy, Mines and Resources Canada. 1985. Canadian Mineral Production 1983 and 1984. Can. Min. J. 106(2): 26-27.

Health and Welfare Canada. 1980. Selenium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 541-554.

Hilton, J.W., P.V. Hodson and S.J. Slinger. 1980. The requirement and toxicity of selenium in rainbow trout (*Salmo gairdneri*). J. Nutr. 110: 2527-2535.

Hodson, P.V., D.J. Spry and B.R. Blunt. 1980. Effects on rainbow trout (*Salmo gairdneri*) of a chronic exposure to waterborne selenium. Can. J. Fish. Aquat. Sci. 37: 233-240.

Hodson, P.V., D.M. Whittle and D. Hallett. 1983. Selenium Contamination of the Great Lakes and its Potential Effects on Aquatic Biota. Manuscript report. Canada Centre for Inland Waters, Burlington, Ontario.

IJC. 1981. Selenium. *In* Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

Kharkar, D.P., K.K. Turekian and K.K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. Geochim. Cosmochim. Acta 32: 285-288.

Lakin, H.W. and D.F. Davidson. 1967. The relation of the geochemistry of selenium to its occurrence in soils. *In* 1st Int. Symp. on Selenium in Biomedicine. O.H. Muth (ed.). AVI Publ. Co., Westport, Connecticut. 445 pp. (Cited in Marier and Jaworski 1983.)

Luttrell, G.W. 1959. Annotated Bibliography on the Geology of Selenium. U.S. Geol. Surv. Bull. No. 1019-M. U.S. Government Printing Office, Washington, D.C.

Marier, J.R. and J.F. Jaworski. 1983. Interactions of Selenium. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 20643. 84 pp.

Nadon, B. and A. Sheffield. 1977. National Inventory of Sources and Emissions of Selenium (1973). Environmental Protection Service, Environment Canada, Ottawa. Rep. No. EPS 3-AP-77-8.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1976. Selenium. Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 203 pp.

Pakkala, I.S., W.H. Gutenmann, D.J. Lisk, G.E. Burdick and E.J. Harris. 1972. A survey of the selenium content of fish from 49 New York State waters. Pestic. Monit. J. 6: 107-114.

Rosenfeld, I. and O.A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicology and Nutrition. Academic Press, New York.

Rudd, J.W.M., M.A. Turner, B.E. Townsend, A. Swick and A. Furutani. 1980. Dynamics of selenium in mercury-contaminated experimental freshwater ecosystems. Can. J. Fish. Aquat. Sci. 37: 848-857.

Sandholm, M., H.E. Oksanen and L. Pesonen. 1973. Uptake of selenium by aquatic organisms. Limnol. Oceanogr. 18: 496-499.

Sato, T., Y. Ose and T. Sakai. 1980. Toxicological effect of selenium on fish. Environ. Pollut. 21A: 217-224.

Shamberger, R.J. 1981. Selenium in the environment. Sci. Total Environ. 17: 59-74.

Stadtman, T.C. 1974. Selenium biochemistry. Science 183: 915-922.

Stahl, Q.R. 1969. Air Pollution Aspects of Selenium and its Compounds. Litton Systems Inc., Maryland. (Cited in Health and Welfare Canada 1980.)

Traversy, W.J., P.D. Goulden, Y.M. Sheikh and J.R. Leacock. 1975. Levels of Arsenic and Selenium in the Great Lakes Region. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. Sci. Ser. No. 58.

Underwood, E.J. 1971. Trace Elements in Human and Animal Nutrition. 3rd edition. Academic Press, New York.

U.S. EPA. 1972. National Inventory of Sources and Emissions. Barium, Boron, Copper, Selenium and Zinc. Section IV. Office of Air Programs, U.S. Environmental Protection Agency, Contract No. 68-02-0100. Leawood, Kansas. 50 pp.

U.S. EPA. 1975. Selenium. *In* Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium and Their Compounds. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1979. Selenium. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 16-1 to 16-13.

U.S. EPA. 1980. Ambient Water Quality Criteria for Selenium. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-070.

Wilber, C.G. 1980. Toxicology of selenium -- A review. Clin. Toxicol. 17: 171-230.

Wood, G.E. 1975. Selenium and tellurium. *In* Canadian Minerals Yearbook 1974. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

6.2.34 Silicon

6.2.34.1 Uses and Production

Silicon metal is used as an alloying agent for aluminum, as the starting material for most semiconductor devices and in the fabrication of silicones, which are used in oil production and the manufacture of numerous products, including synthetic rubber resins, plastomers, antifoaming agents and lubricants (Phillips 1985).

The use of silica (oxidized silicon) in pottery dates back to earliest human history, and in glass to about 12 000 B.C. Industrial uses date from the early 1800's (Kuck 1980). Silica is used in sandblasting, foundry sand, flat glass, container glass, fibreglass, artificial abrasives and smelter flux (Boucher 1985).

The largest user of ferrosilicon is the iron and steel industry, where it is used primarily as a deoxidizer in molten steel (Phillips 1985). Pure silicon has a melting point of 1413°C and dissolves readily in molten metals (Kuck 1980). Silicomanganese, silicocalcium and silicochrome are also used. A third of the Canadian production of ferrosilicon is used in the manufacture of carbon steel. Stainless steel and electric steels contain an average of 10 and 20 $kg{\cdot}t^{-1}$ of steel, respectively (Phillips 1985).

Silica is mined from quartzite deposits in a number of provinces, Quebec and Ontario being the largest producers. Most of the silica imported into Canada comes from the U.S.A. near the Great Lakes (Boucher 1985).

The estimated 1984 production in Canada of quartz and silica sand was 2 624 002 t. Canada imported 767 582 t of silica sand from the U.S.A. and exported 73 565 t of quartzite mostly to the U.S.A. (Boucher 1985). Production, consumption, importation and exportation of silica in Canada are presented in Table 6-46.

Production of silicon metal, ferrosilicon and silicon carbide from silica ores occurs in Quebec and southern Ontario. Silica deposits (SiO_2) are the main commercial source of silicon (Phillips 1985). Only one mine in Canada produced silicon metal (25 000 t) in both 1983 and 1984 (Phillips 1985). Production, consumption, importation and exportation of ferrosilicon in Canada are presented in Table 6-47.

Table 6-46. Production, Consumption, Importation and Exportation of Silica in Canada

Parameter	Compound	Amount (t) 1982	Amount (t) 1983
Production	Quartz and silica sand	1 797 000	2 303 451
Consumption	Quartz and silica sand	2 623 263	NA[1]
Importation	Silica sand	788 768	982 662
	Silex or crystallized quartz	241	271
	Firebrick and similar shapes	2 984	3 027
Exportation	Quartzite	65 333	103 960

[1] NA = not available.

Source: Boucher 1985.

Table 6-47. Production, Consumption, Importation and Exportation of Ferrosilicon in Canada

Parameter	Amount (t) 1982	Amount (t) 1983	Amount (t) 1984
Production	77 089	95 737	90 000
Consumption	46 122	50 022	60 000
Importation	9 860	13 079	NA[1]
Exportation	40 827	45 715	NA[1]

[1] NA = not available.

Source: Phillips 1985.

6.2.34.2 Sources and Pathways for Entering the Aquatic Environment

Silicon is the second most abundant element in the earth's crust. The term "silica" refers to silicon in natural waters, and is usually represented by the hydrated form of the oxide: H_4SiO_4 or $Si(OH)_4$, silicic acid (Faust and Aly 1981). Silica is present in most rocks, but many are resistant to chemical weathering (Faust and Aly 1981). Crystalline quartz (SiO_2) is a major component of many igneous rocks and the grains of sandstones. The major sources of silica in water are the feldspars, micas and clay minerals, or the hydrous aluminum silicates (Faust and Aly 1981). Most sources of silica are natural, but anthropogenic sources include the fluoridation of drinking water and the use of aerosols (McNeely *et al.* 1979).

6.2.34.3 Environmental Concentrations

Most natural waters contain less than 5 $mg{\cdot}L^{-1}$ of silica, although a range of 1-30 $mg{\cdot}L^{-1}$ is not uncommon (McNeely *et al.* 1979). Typical Canadian surface water has a silica concentration of 3-4 $mg{\cdot}L^{-1}$ (McNeely *et al.* 1979). Environmental concentration ranges for silicon and silica in Canadian surface waters are presented in Table 6-48. Groundwater, especially hot springs, may contain as much as 65 $mg{\cdot}L^{-1}$, and

Table 6-48. Environmental Concentration Ranges for Silicon and Silica in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.3[1]-25.4	1481	1980-1985
Western	ND[2,3]-11.7	1104	Prior to 1980
	0.05[1]-40	2901	
Central	ND[1]-12	3897	1980-1985
Atlantic	0.01[1]-24	8006	1980-1985

[1] Detection limit is 0.02 mg·L^{-1} (reactive silica).
[2] ND = not detected.
[3] Detection limit is not stated (ortho solution, silicate).

Source: NAQUADAT 1985.

waters flowing through volcanic rocks may contain silica concentrations exceeding 100 mg·L^{-1}. Silica concentrations in brackish and saline waters may range from 1000 to 4000 mg·L^{-1} (McNeely *et al.* 1979).

6.2.34.4 Forms and Fate in the Aquatic Environment

Silicon is a stable, relatively light chemical element; it does not occur free in nature, but combines with oxygen and other elements to form oxides of silicates (Kuck 1980). Silicon occurs in oxidation states of 0, +2, +3 and +4, with the tetravalent state being the most stable in the aquatic environment. Tetravalent silicon occurs predominantly as insoluble silicate (SiO_2) in equilibrium with silicic acid (H_4SiO_4). Silicic acid is present in small amounts in neutral and slightly alkaline waters, and remains un-ionized up to pH 9. Under alkaline conditions, the solubility of silica becomes enhanced because of the formation of monomeric and polymeric silicates (Stumm and Morgan 1981; Drever 1982).

In natural fresh waters, silicon occurs in two forms: dissolved (H_4SiO_4) and particulate, either suspended in amorphous form or deposited in sediments. The particulate form is associated with biotic material, particularly diatoms and other organisms requiring silicon, and also with inorganic particulates and organic complexes. The formation of silicate complexes with oxides of iron and aluminum effectively removes silicon from the water column above pH 7. Alternatively, solubility is increased by humic compounds and by the formation of iron and aluminum silicate – humic complexes (Wetzel 1975). Interstitial waters are enriched in dissolved silica (silicic acid); concentrations increase below pH 7, decrease between pH 7 and 9, and greatly increase above pH 9. Concentrations also increase at elevated temperatures within the range of limnological interest (Wetzel 1975).

Although relatively unreactive chemically, silicon is considered an essential micronutrient for diatoms; therefore, flux rates of silicon in fresh waters can be significantly influenced by diatom cycling. Diatoms are capable of assimilating large quantities of silicon in the synthesis of frustule cell structures, and, hence, silicon frequently exhibits significant variations in seasonal and spatial distributions in water bodies (Hutchinson 1957; Wetzel 1975). In comparison with abiotic precipitation and sedimentation, assimilation by diatoms with subsequent sedimentation is the predominant mechanism of removal of silicon from the water column.

6.2.34.5 References

Boucher, M.A. 1985. Silica. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 52.1-52.7.

Drever, J.I. 1982. The Geochemistry of Natural Waters. Prentice-Hall Inc., Englewood Cliffs, New Jersey. 388 pp.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

Hutchinson, G.E. 1957. A Treatise in Limnology. Vol. I. Geography, Physics, and Chemistry. John Wiley & Sons, New York. 1015 pp.

Kuck, P.H. 1980. Silicon. *In* Mineral Facts and Problems. U.S. Department of the Interior, Bur. Mines Bull. 671.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Silica. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 51-52.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Phillips, D. 1985. Silicon, ferrosilicon, silicon carbide and fused alumina. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 53.1-53.7.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. 2nd edition. Wiley-Interscience, John Wiley & Sons, New York. 780 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.35 Silver

6.2.35.1 Uses and Production

A large portion of silver consumption is for photographic materials. Other major uses of silver include the manufacture of sterling and plated ware, jewelry, coins and medallions, electrical and electronic products such as batteries, contacts and conductors, brazing alloys and solders, catalysts, mirrors, fungicides and dental and medical supplies. Silver has the highest known electrical and thermal conductivities of all metals. Silver oxide impregnated on charcoal in cartridges may be used as a disinfectant for drinking water (Taylor *et al.* 1980).

Approximately 90% of the annual world production of silver is obtained as a by-product of lead-zinc, copper and gold mining. The remainder comes from deposits that are exploited for silver (Boyle 1968).

Production, consumption, importation and exportation of silver in Canada are presented in Table 6-49. World silver production was estimated at 11 552 t in 1982, 12 130 t in 1983 and 12 700 t in 1984 (Law-West 1985).

6.2.35.2 Sources and Pathways for Entering the Aquatic Environment

Silver is among the less common but most widely distributed elements in the earth's crust. Its average crustal abundance has been estimated at 0.07 mg·kg^{-1}, ranking 69th of 88 elements (Taylor 1964). Silver is a white, lustrous, malleable metal which occurs in nature in elemental form (Cotton and Wilkinson 1980) and in ores such as argentite (Ag_2S), cerargyrite ($AgCl$), proustite ($3AgS \cdot As_2S_3$) and pyrargyrite ($3Ag_2S \cdot Sb_2S_3$) (U.S. EPA 1979).

Natural processes, such as weathering and volcanic activity, release silver to the environment. Silver has been found in various products of fumarolic (hot spring) and volcanic activity associated with sulphur (sulphides, sulphates), chlorides and

Table 6-49. Production, Consumption, Importation and Exportation of Silver in Canada

Parameter	Amount (t) 1982	1983	1984
Production	1314	1106	1168
Consumption	292	180.5	NA[1]
Importation	628	493	181[2]
Exportation	1737	1487	1117[3]

[1] NA = not available.

[2] Partial estimate; data on silver ores and concentrates not available for 1984.

[3] January to September 1984.

Source: Law-West 1985.

Table 6-50. Environmental Concentration Ranges for Total Silver in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<0.005-0.01	69	Prior to 1980
Western	ND[2]	43	Prior to 1980
Atlantic	ND-<0.01	13	Prior to 1980

[1] Detection limit is 0.005-0.01 $mg \cdot L^{-1}$ (total).

[2] ND = not detected.

Source: NAQUADAT 1985.

ammonia salts (Boyle 1968). No estimates of the amount released to the environment via this pathway are available. The amount of silver entering the world's oceans as a result of weathering has been estimated to be 11 000 $t \cdot a^{-1}$ (Bertine and Goldberg 1971).

Various human activities release silver to the environment. An estimated 25% (or 1263 t) of the silver consumed in the U.S.A. annually between 1966 and 1972 was lost to the environment through landfilling, incineration or lagooning, or was discharged directly to water (Smith and Carson 1977). In industrial areas, the silver concentration of surface waters may reach 0.04 $mg \cdot L^{-1}$ (Smith and Carson 1977). Releases of silver to the atmosphere were estimated at 327 t from the iron and steel industry, the cement industry and coal combustion. Silver is also released during the production of crude oil, through the use of silver iodide in cloud seeding for weather modification. Between 0.6 and 0.7 t of silver iodide were used in cloud seeding over western Canada in 1977 (Taylor *et al.* 1980).

6.2.35.3 Environmental Concentrations

Surface waters in nonindustrialized areas contain an estimated 0.3 $\mu g \cdot L^{-1}$ silver (Smith and Carson 1977; NRCC 1982). Sediment lying below these surface waters contained an average of 0.6 $mg \cdot L^{-1}$ silver (Health and Welfare Canada 1980). Measurements for silver recorded at NAQUADAT stations indicated that the silver concentration of 90% of the water samples was below the detection limit, which ranged from 0.004 to 0.01 $mg \cdot L^{-1}$ (NAQUADAT 1978). Environmental concentration ranges for total silver in Canadian surface waters are presented in Table 6-50.

6.2.35.4 Forms and Fate in the Aquatic Environment

Silver exists in oxidation states of 0, +1 and +2; in aqueous systems, ionic silver is primarily in the univalent state, Ag(I). Metallic silver is stable over much of the pH and redox range found in natural waters, but has a very low water solubility (Cotton and Wilkinson 1980). Silver may be present in aquatic systems in colloidal form (e.g. AgCl, Ag_2S, Ag_2Se, Ag_3AsS_3) as an integral part of or adsorbed to various humic substances, or in small amounts as dissolved forms (e.g. as simple silver organic compounds such as tartrates and acetates, or as more complex compounds). In waters containing high concentrations of potassium and sodium chloride, complexes of the form $Na(AgCl_2)$ may be found. Silver may also be dissolved as double complexes of sulphur, arsenic, antimony, tellurium and selenium (Boyle 1968). In waters containing high concentrations of sulphide, complex sulphides and polysulphides may occur. Silver halides are relatively insoluble, and it is considered that the formation of silver chloride plays a major role in the control of aquatic silver mobility where chloride concentrations exceed 35 $mg \cdot L^{-1}$ (Hem 1977).

Under aerobic conditions, the argentous (Ag(I)) ion is soluble and mobile; however, as pH increases, silver tends to precipitate. At pH 7.5-8.0, silver hydrolyzes in aqueous solution as the oxide and becomes insoluble (Boyle 1968). Theoretical equilibrium calculations (Morel *et al.* 1973; Hem 1977; Jenne *et al.* 1978) have shown that in aqueous solution, the predominant silver forms are Ag(I) ion and AgCl. At a concentration of 1 $\mu g \cdot L^{-1}$, 60% of the silver was present as the univalent ion. In the presence of chloride ion, Ag(I) ion concentrations decrease with increasing pH above approximately pH 7. In the absence of chloride, increasing amounts of $Ag(HS)_2^-$ occur with increasing pH. The introduction of complexing agents, such as NTA and citrates, did not significantly alter any of the observed equilibria (Morel *et al.* 1973; Hem 1977; Jenne *et al.* 1978).

Sorption and precipitation are the dominant mechanisms controlling the transport of silver in the aquatic environment. Sorption, particularly by manganese dioxide, and precipitation of silver halides effectively reduce silver concentrations in the water column. The influence of these processes, along with the low crustal abundance of silver, account for its low observed concentrations in the aqueous phase. Redox potential plays an indirect role in silver speciation in that it controls the aqueous behaviour of sulphur and manganese oxides, which in turn control silver speciation (U.S. EPA 1979). Manganese dioxide, followed in turn by $Fe(OH)_3$, montmorillonite, illite, kaolinite and Fe_2O_3, have adsorptive affinities for silver (Kharkar *et al.* 1968). This accounts for the higher reported content of silver in sediments relative to overlying water (Chao and Anderson 1974). Organic material may also adsorb silver. Field studies have shown that the silver content of sediments is correlated with organic content, accounting for enrichment factors up to 10^3 (Freeman 1979).

Photolysis and volatilization are not considered to be important processes in the removal of silver from the water column (U.S. EPA 1979).

Silver may be accumulated by aquatic organisms, although bioconcentration factors are relatively low. For example, bioconcentration factors for algae and *Daphnia magna* were both less than 100 (Terhaar *et al*. 1977). Activated sludge organisms may concentrate silver to 10^3-10^4 times the concentration found in wastewater (Chiu 1973). Largemouth bass (*Micropterus salmoides*) (Coleman and Cearley 1974) and bluegill sunfish (*Lepomis macrochirus*) (Coleman and Cearley 1974; U.S. EPA 1978) accumulated silver to levels generally less than 100 times the concentration in water. A twofold increase in silver content of water lilies (*Nymphaea odorata*) with respect to concentration in water has been reported (Cowgill 1973). Silver does not appear to be subject to biomagnification (Terhaar *et al*. 1977). In addition, biomethylation is unlikely, because of the relative instability of alkyl silver compounds (Cotton and Wilkinson 1980).

6.2.35.5 References

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Boyle, R.W. 1968. The Geochemistry of Silver and its Deposits. Geol. Surv. Can. Bull. No. 160.

Chao, T.T. and B.J. Anderson. 1974. The scavenging of silver by manganese and iron oxides in stream sediments collected from two drainage areas of Colorado. Chem. Geol. 14: 159-166.

Chiu, Y. 1973. Recovery of Heavy Metals by Microbes. Ph.D. Thesis. School of Engineering, University of Western Ontario, London, Ontario.

Coleman, R.L. and J.E. Cearley. 1974. Silver toxicity and accumulation in largemouth bass and bluegill. Bull. Environ. Contam. Toxicol. 12: 53-61.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Cowgill, U.M. 1973. Biogeochemical cycles for the chemical elements in *Nymphaea odorata* Ait. and the aphid *Rhopalosiphum nymphaeae* (L.) living in Linsley Pond. Sci. Total Environ. 2: 259-303.

Freeman, R.A. 1979. Ecological kinetics of silver in an alpine lake ecosystem. *In* Proc. 2nd Annual Symp. Aquatic Toxicology. ASTM STP 667. L.L. Marking and R.A. Kimerle (eds.). American Society for Testing and Materials, Cleveland, Ohio. pp. 342-358.

Health and Welfare Canada. 1980. Silver. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 555-562.

Hem, J.D. 1977. Reactions of metal ions at surfaces of hydrous iron oxide. Geochim. Cosmochim. Acta 41: 527-538.

Jenne, E.A., D.C. Grivin, J.W. Ball and J.M. Barchard. 1978. Inorganic speciation of silver in natural waters – fresh to marine. *In* Environmental Impacts of Artificial Ice Nucleating Agents. D.A. Klein (ed.). Dowden, Hutchinson and Ross Inc., Stroudsburg, Pennsylvania. pp. 41-61. (Cited in Taylor *et al*. 1980.)

Kharkar, D.P., K.K. Turekian and K.K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. Geochim. Cosmochim. Acta 32: 285-298.

Law-West, D. 1985. Silver. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 54.1-54.10.

Morel, F., R.E. McDuff and J.P. Morgan. 1973. Interactions and chemostasis in aquatic systems: role of pH, pE, solubility and complexation. *In* Trace Metals and Metal-Organic Interactions in Natural Waters. P.C. Singer (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 157-200. (Cited in Taylor *et al*. 1980.)

NAQUADAT. 1978. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1982. Data Sheets on Selected Toxic Elements. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 19252. 61 pp.

Smith, I.C. and B.L. Carson. 1977. Trace Metals in the Environment. Vol. 2. Silver. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 469 pp.

Taylor, M.C., A. Demayo and S. Reeder. 1980. Silver. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28: 1273-1285.

Terhaar, C.J., W.S. Ewell, S.P. Dziuba, W.W. White and P.J. Murphy. 1977. A laboratory model for evaluating the behavior of heavy metals in an aquatic environment. Water Res. 11: 101-110.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency, Washington, D.C. EPA Contract No. 68-01-4646.

U.S. EPA. 1979. Silver. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 17-1 to 17-11.

U.S. EPA. 1980. Ambient Water Quality Criteria for Silver. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-071.

6.2.36 Sodium

6.2.36.1 Uses and Production

Sodium is produced in Canada primarily as sodium chloride (salt or halite) and sodium sulphate (salt cake) (Health and Welfare Canada 1980; Ontario Ministry of the Environment 1981; Barry 1985; Prud'homme 1985). Sodium sulphate is used mainly in the pulp and paper, glass and glass-wool and soap industries. Smaller amounts of sodium sulphate are used in the manufacture of pigments and colours, medicinals and industrial chemicals, in base metal smelting and as a mineral feed supplement (Health and Welfare Canada 1980; Ontario Ministry of the Environment 1981; Barry 1985).

Canadian consumption of sodium chloride and sodium sulphate is presented in Table 6-51. Sodium chloride is also used in the production of caustic soda, chlorine, and sodium carbonate, chlorate, chlorite, bicarbonate and hypochlorite (Health and Welfare Canada 1980; Prud'homme 1985). Other uses include food processing, slaughtering and meat packing and dairy, fishing and the grain and brewing industries (Prud'homme 1985). Some commercial water-softening devices also use sodium (Ontario Ministry of the Environment 1981).

Production, importation and exportation of salt (sodium chloride), sodium sulphate and sodium phosphates in Canada are presented in Table 6-52.

6.2.36.2 Sources and Pathways for Entering the Aquatic Environment

Sodium is the sixth most abundant element on earth and constitutes 2.6% of the earth's crust (Ontario Ministry of the Environment 1981). All natural waters contain some sodium

Table 6-51. Consumption of Salt (Sodium Chloride) and Sodium Sulphate in Canada

	Amount (t)			
Compound/use	1980	1981	1982	1983
Salt				
Snow and ice control	2 472 849	3 001 260	3 088 315	2 712 088
Industrial chemicals	2 974 520	3 234 020	2 966 218	3 495 000
Fishing industry	65 000	68 000	83 000	64 000
Food processing				
Fruit and vegetable processing	20 619	19 168	18 008	22 300
Bakeries	15 017	14 079	13 746	16 300
Fish products	24 296	33 983	33 582	35 200
Dairy products	13 056	10 740	10 447	12 900
Biscuits	1 892	2 022	2 082	2 600
Miscellaneous food preparation	46 587	24 874	22 680	36 000
Grain mills	77 412	67 036	63 899	79 000
Slaughtering and meat processing	45 611	44 725	37 347	49 000
Pulp and paper mills	28 980	25 344	38 939	35 200
Leather tanneries	7 346	9 964	7 708	9 500
Miscellaneous textiles	2 924	2 664	2 871	3 400
Breweries	294	352	279	300
Other manufacturing industries	8 732	10 492	7 923	10 300
Total	5 805 135	6 568 723	6 397 044	6 583 088
Sodium sulphate				
Pulp and paper	NA[1]	158 927	142 281	141 172
Soaps	NA	40 855	38 437	40 219
Glass	NA	NA	NA	9 551
Glass-wool	NA	12 001	11 286	NA
Colours, pigments, feed supplements, etc.	NA	4 515	3 337	676
Total	NA	216 298	195 341	191 618

[1] NA = not available.

Sources: Barry 1985; Prud'homme 1985.

Table 6-52. Production, Importation and Exportation of Salt (Sodium Chloride), Sodium Sulphate and Sodium Phosphates in Canada

		Amount (t)		
Parameter	Compound	1982	1983	1984
Production	Sodium chloride	7 972 644	8 591 000	10 294 000[1]
	Sodium sulphate	547 000	453 939	386 600
	Sodium phosphates	55 000	56 500	59 500
Importation	Salt, wet in bulk	372 536	277 834	368 217
	Salt, domestic	8 877	8 277	7 351
	Salt (group not specified)	1 145 466	528 139	399 606
	Salt and brine	1 526 879	814 250	775 174
	Salt cake (sodium sulphate) and Glauber's salt	17 293	22 479	16 229
	Sodium phosphates	4 600	5 500	6 900
Exportation	Salt and brine	1 721 893	1 914 629	1 870 750
	Crude sodium sulphate	367 924	265 752	170 799
	Sodium phosphates	6 000	6 000	5 600

[1] Energy, Mines and Resources Canada 1985.

Sources: Barry 1985; Prud'homme 1985; CORPUS Information Services 1985.

(McNeely *et al.* 1979; Ontario Ministry of the Environment 1981). Water in contact with igneous rocks provides a natural source of sodium, although the principal source in the aquatic environment is the weathering of salt deposits (Ontario Ministry of the Environment 1981). The major sodium-bearing minerals are soda feldspars, feldspathoids and evaporitic minerals, such as halite (NaCl) and thenardite (Na_2SO_4) (Faust and Aly 1981).

Soils high in sodium content can result in increased groundwater concentrations through leaching, and perhaps increase the salinity of rivers and streams. Most soils contain 0.1-1% sodium, mainly as such silicate minerals as amphiboles and feldspars (Bowser *et al.* 1962).

About 25-50% of the salt used on roads to control snow and ice enters the groundwater and, along with the increased levels from runoff in soils, may result in elevated concentrations in water supplies (McConnell and Lewis 1972). Elevated levels in surface water may also result from sewage and industrial effluents, the intrusion of seawater into coastal areas and the use of sodium compounds for corrosion control and water softening. Smaller quantities of sodium in the aquatic environment may result from the use of sodium hypochlorite for disinfection and sodium fluoride for fluoridation of water for the control of dental caries (Health and Welfare Canada 1980).

6.2.36.3 Environmental Concentrations

The concentration of sodium in natural waters varies considerably, and may range from below 1 mg·L^{-1} to 10^5 mg·L^{-1} in brines (McNeely *et al.* 1979; Ontario Ministry of the Environment 1981), depending on the source of sodium, the regional and local hydrological and geological conditions, the time of year and salt utilization patterns (Health and Welfare Canada 1980). The underground salt deposits of Saskatchewan, Alberta, Nova Scotia and southwestern Ontario and the naturally occurring brines of southern Alberta and Saskatchewan lakes are major sources of sodium in Canada (Prud'homme 1985).

A mean sodium concentration of 9 mg·L^{-1} was estimated for North American river waters (Altman and Dittmer 1966). Sodium concentrations in the Great Lakes vary from an average of 1.3 mg·L^{-1} in Lake Superior to approximately 12-13 mg·L^{-1} in Lake Ontario (Dobson 1967; Weiler and Chawla 1969). This difference is a result of increased sodium input from industrial sources and road salting. Concentrations of sodium downstream from Lake Huron in the Great Lakes are steadily increasing with time (IJC 1969). The Atlantic region was the only region to report total sodium on NAQUADAT; the concentration was 2.7-5.9 mg·L^{-1} (detection limit 0.2 mg·L^{-1} total sodium) based on seven samples taken prior to 1980 (NAQUADAT 1985).

Groundwater sodium concentrations are somewhat higher than surface water concentrations. A range of 6-130 mg·L^{-1} sodium may be found in groundwater, although concentrations will be higher in saline soils (Bond and Straub 1973). Seawater contains sodium concentrations of about 10 500 mg·L^{-1}. In brines, the concentration may range from 25 to 100 g·L^{-1} (McNeely *et al.* 1979).

6.2.36.4 Forms and Fate in the Aquatic Environment

Sodium is found in the ionic form in all surface waters (Wetzel 1975). Nearly all sodium salts are readily water-soluble and tend to remain in aqueous solution. Because there are few sodium salts that are not appreciably water-soluble, there are no important precipitation or adsorption reactions of the aqueous ion (Cotton and Wilkinson 1980).

Sodium is essential to some microorganisms and plants and to all animals; hence, it is readily bioaccumulated. Concentrations in various organisms have been reported, e.g. 26 000-41 000 mg·kg^{-1} in marine algae; 8000 mg·kg^{-1} in marine fish; 35-1500 mg·kg^{-1} in terrestrial vegetation; 2-2400 mg·kg^{-1} in edible vegetables; and 2600-7800 and 10 000 mg·kg^{-1} in mammalian muscle and bone, respectively (Bowen 1979).

6.2.36.5 References

Altman, P.L. and D.S. Dittmer (eds.). 1966. Mineral nutrients in lake and river waters. *In* Environmental Biology. Federation of American Societies for Experimental Biology, Bethesda, Maryland. 694 pp. (Cited in Health and Welfare Canada 1980.)

Barry, G.S. 1985. Sodium sulphate. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 55.1-55.5

Bond, R.G. and C.P. Straub. 1973. Genetic types of subterranean waters in relation to their salinity. *In* Handbook of Environmental Control. Vol. 3. Water Supply and Treatment. 1st edition. Chemical Rubber Co., Cleveland, Ohio. p. 85. (Cited in Health and Welfare Canada 1980.)

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Bowser, W.E., R.A. Milne and R.R. Cairns. 1962. Characteristics of the major soil groups in an area dominated by solonetzic soils. Can. J. Soil Sci. 42: 165-179.

CORPUS Information Services. 1985. Sodium phosphates (dibasic DSP; tribasic TSP; tetrabasic pyro; tripoly or STPP; meta). CPI Product Profile. Don Mills, Ontario.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Dobson, H.H. 1967. Principal ions and dissolved oxygen in Lake Ontario. *In* Proc. 10th Conf. on Great Lakes Research, April 10-12, Toronto, Ontario. pp. 337-356.

Energy, Mines and Resources Canada. 1985. Canadian mineral production 1983 and 1984. Can. Min. J. 106(2): 26-27.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

Health and Welfare Canada. 1980. Sodium. *In* Guidelines for Canadian Drinking Water 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 563-576.

IJC. 1969. Pollution of Lake Ontario and the International Section of the St. Lawrence River. Vol. 3. Report by the International Lake Erie Water Pollution Board/the International Lake Ontario – St. Lawrence River Water Pollution Board, International Joint Commission, Windsor, Ontario.

McConnell, H.H. and J. Lewis. 1972. Add salt to taste. Environment 14(9): 38-45.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Sodium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 53.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Prud'homme, M. 1985. Salt. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 50.1-50.9.

Weiler, R.R. and V.K. Chawla. 1969. Dissolved mineral quality of Great Lakes waters. *In* Proc. 12th Conf. on Great Lakes Research, May 5-7, Ann Arbor, Michigan. pp. 801-818.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.37 Sodium Adsorption Ratio

The Sodium Adsorption Ratio (SAR) is used to evaluate the suitability of waters used for agricultural irrigation. The ratio is an estimate of the degree to which sodium will be adsorbed from water by soil. It is calculated from the ionic concentration of sodium, calcium and magnesium according to the following equation:

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\dfrac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}}$$

where the concentrations of sodium, calcium and magnesium are expressed in milliequivalents per litre. The SAR evaluates the potential base exchange relationships in which calcium and magnesium in a soil are replaced by sodium present in irrigation water (McNeely *et al.* 1979).

6.2.37.1 References

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Sodium adsorption ratio. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 53-55.

6.2.38 Sulphur

6.2.38.1 Introduction

Sulphur occurs in a number of oxidation states, ranging from −2 to +6, in the natural environment. The most abundant forms of sulphur have oxidation states of +6 (sulphates, sulphate esters), 0 (elemental sulphur) and −2 (sulphides, reduced organic sulphur). Sulphur dioxide and sulphites (+4) and polysulphur compounds having mixed oxidation states, such as thiosulphates and polythionates, are considered to be transient forms in the global biogeochemical cycling of sulphur (Trudinger 1979; Krouse and McCready 1979). The overall biogeochemical cycling of sulphur includes chemical and biological transformations of the different forms of sulphur and their transfer among atmospheric, hydrospheric, biospheric and pedospheric reservoirs (Granat *et al.* 1976; Krouse and McCready 1979). Anthropogenic and biogenic inputs are considered important in the various reservoirs of the cycle. Sulphur cycling in fresh waters has been extensively studied and relatively well-defined (Hutchinson 1957; Goldhaber and Kaplan 1974; Wetzel 1975). In 1984, 6 998 000 t of sulphur were produced in Canada. Importation was only 3 t, and consumption was 873 000 t. Canada is currently the world's largest exporter of sulphur, at 6 128 000 t in 1984, with 15% being shipped to the U.S.A. (CORPUS Information Services 1985).

Sulphur, in the form of cysteine, methionine and other organic compounds, is an essential component of living matter; hence, all organisms play a role in sulphur cycling. Sulphate (SO_4^{2-}) is considered to be the predominant form of sulphur in aerobic environments. Nearly all assimilation of sulphur by eucaryotes occurs as sulphate. Sulphate is reduced to the sulphydryl (−SH) form during protein synthesis in plant and animal metabolism. The decomposition of organic matter by heterotrophic bacteria is accompanied by a reduction to sulphide (S^{2-}) compounds. In addition, a number of heterotrophic, anaerobic bacteria are capable of reducing sulphate, sulphite, thiosulphate, hyposulphate and elemental sulphur to sulphide, primarily as hydrogen sulphide (H_2S). Under aerobic conditions, however, most H_2S is rapidly oxidized. Several groups of bacteria are capable of oxidizing sulphide to elemental sulphur and sulphate (Hutchinson 1957; Goldhaber and Kaplan 1974; Wetzel 1975).

6.2.38.2 References

CORPUS Information Services. 1985. Sulfur (brimstone). CPI Product Profile. Don Mills, Ontario.

Goldhaber, M.B. and I.R. Kaplan. 1974. The sulfur cycle. *In* The Sea. Ideas and Observations on Progress in the Study of the Seas. E.D. Goldberg (ed.). John Wiley & Sons, New York. pp. 569-655.

Granat, L., R.O. Hallberg and H. Rodke. 1976. The global sulfur cycle. *In* Nitrogen, Phosphorus and Sulfur – Global Cycles. SCOPE Report 7. B.H. Svensson and R. Söderlund (eds.). Ecological Bulletins No. 22. Swedish Natural Science Research Council, Stockholm, Sweden. pp. 89-134.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, New York. 1015 pp.

Krouse, H.R. and R.G.L. McCready. 1979. Biogeochemical cycling of sulfur. *In* Biogeochemical Cycling of Mineral-forming Elements. P.A. Trudinger and D.J. Swaine (eds.). Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. pp. 401-430.

Trudinger, P.A. 1979. The biological sulfur cycle. *In* Biogeochemical Cycling of Mineral-forming Elements. P.A. Trudinger and D.J. Swaine (eds.). Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. pp. 293-313.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.38.3 Sulphate

6.2.38.3.1 Uses and Production

The uses of sulphate include the manufacture of chemicals, dyes, fertilizers, glass, paper, pottery and porcelain, soaps, detergents, textiles, dough conditioners, fungicides, bactericides, astringents and emetics. The mining, pulping, electro- and nickel-plating industries use sulphate, and it is also used in sewage treatment and wood preservation (McKee and Wolf 1963; Little (Arthur D.), Inc. 1971; Barry 1985a).

The sodium sulphate industry is the primary sulphate-producing industry in Canada, and is based in southern Saskatchewan and Alberta, where natural brine deposits occur (Health and Welfare Canada 1980; Barry 1985a).

In 1982, 547 000 t of sodium sulphate were produced in Canada whereas 17 293 t were imported. Besides natural sodium sulphate, about 90 000 $t \cdot a^{-1}$ are produced as a by-product of industrial and chemical processes in central Canada (Barry 1985a). The Canadian consumption of sulphate in 1982 was 195 341 t, 73% of which was used by kraft pulp and paper mills (Barry 1985a); 15 400 t of potassium sulphate were imported into Canada in 1983 for use in fertilizers (Barry 1985b).

6.2.38.3.2 Sources and Pathways for Entering the Aquatic Environment

Sulphates may be leached from most sedimentary rocks, including shales, with the most appreciable contributions from such sulphate deposits as gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$). Upon oxidation, organic materials may contribute sulphates to waters (McNeely *et al.* 1979).

Industrial discharges to the aquatic environment are a significant source of sulphates. Tanneries, sulphite-pulp mills, textile plants, sulphuric acid plants, some metalworking industries and mine drainage wastes are all sources of sulphate input to receiving waters. Industrial processes, such as the combustion of coal and the roasting of sulphur-containing ores, can emit large amounts of sulphur dioxide and sulphur trioxide to the atmosphere, and are responsible for adding sulphates to surface waters through precipitation. Precipitation and subsequent leaching supplies nearly all the sulphate of surface waters in the crystalline rock areas of North America. Dry deposition of sulphates is also a source of input to surface waters (McNeely *et al.* 1979; Health and Welfare Canada 1980; Ontario Ministry of the Environment 1981; NRCC 1981).

The primary source of sulphate in rain and snow in nonindustrialized areas is through atmospherically oxidized H_2S, which is produced along coastal regions by anaerobic bacteria (NRCC 1981).

6.2.38.3.3 Environmental Concentrations

Sulphate is widely distributed in nature, and is an ionic component of water. Sulphate concentrations normally vary from 10 to 80 mg·L^{-1} in surface waters, although they may reach several thousand milligrams per litre near some industrial discharges (Ontario Ministry of the Environment 1981). Industrial wastewater from one station in British Columbia reported maximum concentrations of 1010-2490 mg·L^{-1} in four samples taken in 1980 (NAQUADAT 1985). High sulphate concentrations are present in some well waters and surface waters in arid regions where sulphate minerals are present. Waters in areas of acid mine drainage may also have elevated concentrations (McNeely *et al.* 1979).

Sulphate concentrations in some Canadian lakes range from 3 to 30 mg·L^{-1} (Katz 1977). Canadian water supplies surveyed between 1966 and 1974 contained less than 58 mg·L^{-1} sulphate in 96% of the 71 municipal water supplies sampled (NAQUADAT 1977). Environmental concentration ranges for sulphate in Canadian surface waters are presented in Table 6-53.

Brines exhibit concentrations of 200 000 mg·L^{-1}, and seawater contains about 2700 mg·L^{-1} (Hitchcock 1975). Rainwater in Canada normally contains 1-2 mg·L^{-1} sulphate (Katz 1977).

6.2.38.3.4 Forms and Fate in the Aquatic Environment

Sulphate (SO_4^{2-}) is the stable, oxidized form of sulphur and is readily soluble in water. Lead, barium and strontium sulphates, however, are insoluble. Dissolved sulphate may be reduced to sulphide and volatilized to the atmosphere as H_2S, precipitated as insoluble salts or incorporated in living organisms. Sulphates serve as an oxygen source for bacteria, under anaerobic conditions, which convert it to hydrogen sulphide. Sulphate can be produced by the bacterial oxidation of reduced sulphur compounds, including metallic sulphides and organosulphur compounds (Hutchinson 1957; Goldhaber and Kaplan 1974; Wetzel 1975).

Table 6-53. Environmental Concentration Ranges for Sulphate in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	ND[2]-820.0	1 554	1980-1985
Western	ND-3040.0	3 149	1980-1985
Central	ND-77.3	4 696	1980-1985
Atlantic	ND-610.0	13 646	1980-1985

[1] Detection limit is 1.0 mg·L^{-1} (dissolved).
[2] ND = not detected.

Source: NAQUADAT 1985.

6.2.38.3.5 References

Barry, G.S. 1985a. Sodium sulphate. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 55.1-55.5.

Barry, G.S. 1985b. Potash. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 47.1-47.15.

Goldhaber, M.B. and I.R. Kaplan. 1974. The sulfur cycle. *In* The Sea. Ideas and Observations on Progress in the Study of the Seas. E.D. Goldberg (ed.). John Wiley & Sons, New York. pp. 569-655.

Health and Welfare Canada. 1980. Sulphate. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 577-585.

Hitchcock, D.R. 1975. Biogenic contribution to atmospheric sulfate levels. *In* Proc. 2nd Natl. Conf. on Complete Water Re-use. Am. Inst. Chem. Eng., and EPA Technol. Transfer, Chicago, Illinois. pp. 291-310.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, New York. 1015 pp.

Katz, M. 1977. The Canadian sulphur problem. *In* Sulphur and Its Organic Derivatives in the Canadian Environment. National Research Council of Canada, Ottawa. NRCC No. 15015. pp. 21-67.

Little (Arthur D.), Inc. 1971. Water Quality Criteria Data Book. Vol. II. Inorganic Chemical Pollution of Freshwater. Water Pollution Control Research Series No. DPV 18010. U.S. Environmental Protection Agency, Washington, D.C.

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. Resources Agency of California, State Water Resources Control Board. pp. 136, 213, 247, 270, 275-277.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Sulphate. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 57.

NAQUADAT. 1977. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1981. Acidification in the Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18475. 369 pp.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.38.4 Sulphide – Hydrogen Sulphide

6.2.38.4.1 Uses and Production

Hydrogen sulphide and other soluble sulphides are used in pigment and dye manufacturing, tanning, chemical processing and the production of cosmetics (Keenan *et al.* 1976; Health and Welfare Canada 1980). Dimethyl sulphide is used as a constituent of artificial flavouring agents (Butterworth *et al.* 1975). Water containing elevated concentrations of hydrogen sulphide is used for therapeutic baths and has been consumed for medicinal purposes (Health and Welfare Canada 1980). Hydrogen sulphide is also used commercially in the manufacture of heavy water, to purify hydrochloric and sulphuric acids, to precipitate sulphides of metals and to manufacture elemental sulphur, mercaptans, ethylene, nylon, soda ash, sodium hydrosulphide and other materials. It is used as a reducing agent in cresylic acid recovery and as a reagent in analytical chemistry (Environment Canada 1984).

In 1981 and 1982, 3178 and 2902 t, respectively, of hydrogen sulphide were manufactured in Canada (Statistics Canada 1984). Importation data for 1981 and 1982 for sulphide compounds are presented in Table 6-54.

Table 6-54. Importation of Several Sulphide Compounds into Canada

Compound	Amount (t) 1981	1982
Carbon sulphides	12	19
Phosphorus pentasulphide	118	121
Phosphorus sulphides (excluding pentasulphide)	2	1
Silicon sulphides	1	—
Hydrogen sulphide	1342	1453

Source: Statistics Canada 1983.

6.2.38.4.2 Sources and Pathways for Entering the Aquatic Environment

Sources of sulphur compounds to natural waters include geochemical weathering, fertilizers and atmospheric deposition. Atmospheric sources, augmented greatly by combustion products of industry, dominate all other sources (Wetzel 1975).

Sulphide is formed by bacterial reduction of sulphate and organic sulphur compounds under anaerobic conditions. It is, therefore, commonly found in domestic and industrial wastewater, sludges, the hypolimnion of stratified lakes and other aquatic systems where anaerobic conditions prevail (Ontario Ministry of the Environment 1981). Reduced sulphur, as H_2S, is added in large quantities to the atmosphere from volcanic gases and biogenic and industrial sources (Kuznetsov 1964; Kellogg *et al.* 1972; NRCC 1981).

6.2.38.4.3 Environmental Concentrations

Total sulphide concentrations as high as 0.7 $mg \cdot L^{-1}$ have been reported in bottom sludge deposits of surface waters, and concentrations of 0.02-0.1 $mg \cdot L^{-1}$ are common in the first 20 mm of the water column above these sludge layers (McNeely *et al.* 1979). In the Rainy River, along the border between Ontario and Minnesota, the mean hydrogen sulphide concentration was 0.07 $mg \cdot L^{-1}$ within 20 mm of the bottom of sludge beds, and ranged from nondetectable to 0.06 $mg \cdot L^{-1}$ at the surface (Colby and Smith 1967). Groundwater usually contains little or no sulphide, because metal sulphides have low solubility and are usually precipitated from solution (McNeely *et al.* 1979). Environmental concentration ranges for sulphide in Canadian surface waters are presented in Table 6-55.

Table 6-55. Environmental Concentration Ranges for Sulphide in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Western	1.0-11.0	46	1980-1982
Atlantic	1.0	3	Prior to 1980
Central	14.0	1	Prior to 1980

[1] Detection limit is 0.001 $mg \cdot L^{-1}$.

Source: NAQUADAT 1985.

Some brines, especially those associated with petroleum deposits, may contain several hundred milligrams of dissolved hydrogen sulphide per litre (McNeely *et al.* 1979).

6.2.38.4.4 Forms and Fate in the Aquatic Environment

Sulphate is considered to be the predominant form of sulphur in aerobic environments. Nearly all assimilation of sulphur is as sulphate in water, but during the decomposition of organic matter sulphur is released largely as hydrogen sulphide (H_2S). Under aerobic conditions hydrogen sulphide is oxidized rapidly. Hence, under aerobic conditions in aquatic systems, concentrations of hydrogen sulphide would be very low (Hutchinson 1957; Wetzel 1975).

Although sulphate and H_2S dominate, HS^- and very small concentrations of S^{2-} occur in strongly alkaline solutions, because H_2S, which is soluble in water, dissociates weakly ($K_1 = 10^{-7}$; $K_2 = 10^{-15}$) (Hutchinson 1957; Hem 1960). Under certain conditions of low redox and pH, in which partial oxidation of sulphides occurs, elemental sulphur may be formed (Wetzel 1975).

Metal sulphides are insoluble at neutral or alkaline pH values. Ferrous iron released from sediments in anaerobic lakes combines readily with H_2S to form insoluble FeS. Appreciable accumulation of H_2S will occur in an anaerobic hypolimnion that is slightly acidic. If the water is alkaline, H_2S will accumulate only after most of the ferrous iron has been precipitated as FeS. The removal of sulphide by the release of ferrous iron will permit an increase in the migration of other metals from the sediments, such as Cu, Zn and Pb, which form even more insoluble sulphides than that of FeS. Oxidation-reduction reactions involving sulphur play a significant role in the modification of conditions for numerous other nutrients, especially for the mobilization of phosphate in freshwater systems (Wetzel 1975).

Sulphur of black sediments of eutrophic lakes consists of sulphide dissolved in interstitial water, acid-soluble sulphide, elemental sulphur, organic sulphur and sulphates (Nriagu 1968; Wetzel 1975).

6.2.38.4.5 References

Butterworth, K.R., F.M.B. Carpanini, I.F. Gaunt, J. Hardy, I.S. Kiss and S.D. Gangolli. 1975. Short-term toxicity of dimethyl sulfide in the rat. Food Cosmet. Toxicol. 13: 15-22. (Cited in Health and Welfare Canada 1980.)

Colby, P.J. and L.L. Smith, Jr. 1967. Survival of walleye eggs and fry on paper fibre sludge deposits in Rainy River, Minnesota. Trans. Am. Fish. Soc. 96: 278-296.

Environment Canada. 1984. Hydrogen Sulphide. Environmental and Technical Information for Problem Spills (EnviroTIPS). Environmental Protection Service, Ottawa.

Health and Welfare Canada. 1980. Sulphide. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 587-596.

Hem, J.D. 1960. Some chemical relationships among sulfur species and dissolved ferrous iron. *In* Chemistry of Iron in Natural Water. U.S. Geol. Surv. Water Supply Pap. 1459-C. pp. 57-73.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, New York. 1015 pp.

Keenan, C.W., J.H. Wood and D.C. Kleinfelter. 1976. General College Chemistry. 5th edition. Harper and Row Publ., New York. p. 563. (Cited in Health and Welfare Canada 1980.)

Kellogg, W.W., R.D. Cadle, E.R. Allen, A.L. Lazrus and E.A. Martell. 1972. The sulfur cycle. Science 175: 587-596.

Kuznetsov, S.I. 1964. Biogeochemistry of Sulfur. *In* Atti. Simp. Intern. Agrochim., Palermo, Italy. Vol. 5. pp. 312-330. (Cited in Wetzel 1975.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Sulphide – hydrogen sulphide. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 57-58.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1981. Hydrogen Sulphide in the Atmospheric Environment. Scientific Criteria for Assessing Its Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18467. 196 pp.

Nriagu, J.O. 1968. Sulfur metabolism and sedimentary environment: Lake Mendota, Wisconsin. Limnol. Oceanogr. 13: 430-439.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Industrial and Agricultural Chemical Products 1982. Annual Census of Manufacturers. Catalogue No. 46-224.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.2.39 Thallium

6.2.39.1 Uses and Production

Thallium compounds are used in the manufacture of alloys (U.S. EPA 1980), electrical apparatus, catalysts for industrial organic reactions and optical equipment (e.g. spectrometers), and in photographic and ceramic formulations (NRCC 1982). For example, thallium sulphide is used in photocells; thallium bromide-iodide crystals are used as infrared detectors; thallium with sulphur or selenium and arsenic and thallium oxide are used to produce special glasses; and other thallium compounds are used as depilatories, dyes and pigments (McNeely *et al.* 1979). Thallium salts have been used successfully for the treatment of ringworm and other skin infections. Thallous acetate has been used in the treatment of dysentery and tuberculosis (U.S. Department of the Interior 1980). The most recent data on Canadian thallium refinery production were for 1978, when 1.36 t were produced (U.S. Department of the Interior 1980). Importation data on thallium and thallium alloys are presented in Table 6-56.

Table 6-56. Importation of Thallium and Thallium Alloys into Canada

	Amount (t)	
Compound	1982	1983
Thallium primary forms and fabricated material	668	1202
Thallium alloys primary forms and fabricated material	17	4

Sources: Statistics Canada 1983, 1984.

6.2.39.2 Sources and Pathways for Entering the Aquatic Environment

The average concentration of thallium in the earth's crust is 0.3-0.6 mg·kg^{-1} (NRCC 1982). Some thallium minerals occur in nature but are rare, e.g. crookesite, hutchinsonite, lorandite and avicennite. Thallium is also found in potassium minerals, such as feldspars and micas; it occurs as a component of independent minerals and as a substitute element in minerals such as galena (U.S. EPA 1979).

The main natural source by which thallium is released into the environment is weathering, with an estimated 2400 t·a^{-1} of thallium entering the environment globally (NRCC 1982).

Thallium is introduced into the aquatic environment as waste from the production of other metals, e.g. from the roasting of pyrite during the production of sulphuric acid, and in mining and smelting operations of copper, gold, zinc, lead and cadmium (McNeely *et al.* 1979). Concentrations ranging from 7 to 88 µg·L^{-1} were reported in discharge streams from Canadian ore operations (U.S. EPA 1980). It has been estimated that the global mobilization of thallium by mining processes is 30 t·a^{-1}, whereas combustion by oil and coal mobilizes 54 t·a^{-1} (NRCC 1982).

6.2.39.3 Environmental Concentrations

Thallium is present in trace amounts in fresh water (McNeely *et al.* 1979). The Pacific region was the only region to report thallium concentrations (as total) on NAQUADAT. The concentration range was 0.0052-0.1 mg·L^{-1} (detection limit 5 µg·L^{-1} total) based on three samples taken prior to 1980 (NAQUADAT 1985).

Concentrations of thallium in other environmental media and organisms have also been reported: soil, 0.2 mg·kg^{-1}, with a range of 0.1-0.8 mg·kg^{-1}; urban dust, 0.07-6 mg·kg^{-1}; vascular plants, 0.03-0.3 mg·kg^{-1}; and fish (soft tissue), 0.08 mg·kg^{-1}. In the human body, which has a total body burden of 0.1-0.5 mg thallium, muscle contains the highest concentrations (NRCC 1982).

6.2.39.4 Forms and Fate in the Aquatic Environment

Thallium exists in oxidation states of 0, +1 and +3; the thallous ion, Tl(I), forms relatively few complexes, whereas the thallic ion, Tl(III), occurs in several organometallic compounds (Cotton and Wilkinson 1980).

The major fates of thallium in the aquatic environment are transport as soluble complexes, sorption to clay minerals and bioaccumulation; the behaviour of thallium in natural water is, however, not well documented (U.S. EPA 1979). In reducing environments, thallium may be precipitated in the elemental form or, in the presence of sulphur, as the insoluble sulphide (Lee 1971; Magorian *et al.* 1974). In waters of high oxygen content, some Tl(III) may be present, but Tl(I) is the predominant form of thallium in most aerobic natural waters (U.S. EPA 1979). Chloride, carbonate and hydroxy salts of Tl(I) are soluble, whereas the sulphide is not (Smith and Carson 1977). Soluble thallic compounds may be hydrolyzed to form colloidal oxides in natural waters (Cotton and Wilkinson 1980), which may then precipitate onto sediments; reducing conditions in sediments will yield Tl(I) which, in the presence of sulphide, forms insoluble Tl_2S (Lee 1971). Thallium-inorganic and thallium-organic ligand interactions are affected by pH. As the pH decreases from 9.1 to 6.2, thallium – humic acid complexation decreases to zero at pH 7.2 and below. Alternatively, as pH increases from 6.2 to 9.1, thallium-inorganic interactions decrease (O'Shea and Mancy 1979).

Thallium is strongly sorbed by montmorillonite clay; at pH 8.1, over 95% of the thallium (100 $\mu g \cdot L^{-1}$) was removed from the water column by the clay, hectorite (1 $g \cdot L^{-1}$), within 24 h. At pH 4, however, sorption was not effective in thallium removal (Magorian *et al.* 1974). In a study of heavy metal cycling in a lake in southwestern Michigan, thallium was detected only in the sedimentary phase (Mathis and Kevern 1975).

Thallium may be bioaccumulated. The alga *Ulothrix* sp. concentrated thallium 127-220 times the concentration found in water within 24 h (Magorian *et al.* 1974). Bioconcentration factors as high as 10^6 have been reported for freshwater plants, invertebrates and fish (Chapman *et al.* 1968). Bluegills (*Lepomis macrochirus*) had a bioconcentration factor of 34 (whole body) after exposure to thallium for 28 d (U.S. EPA 1978). The muscle tissue of juvenile Atlantic salmon (*Salmo salar*) attained a bioconcentration factor of 130 after a 12.5-d exposure (Zitko *et al.* 1975). Exposure of bluegill sunfish (*Lepomis macrochirus*) to 80 $\mu g \cdot L^{-1}$ thallium (as Tl_2SO_4) for 28 d resulted in a concentration factor of 34; the half-life of thallium in tissues was longer than 4 d (Barrows *et al.* 1980). The biomethylation of thallium has been demonstrated; $(CH_3)_2Tl^+$ was formed from Tl(III) ion in anaerobic bacterial cultures (Huber *et al.* 1978).

6.2.39.5 References

Barrows, M.E., S.R. Petrocelli, K.J. Macek and J.J. Carroll. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 379-392.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

Huber, F., U. Schmidt and H. Kirchmann. 1978. Aqueous chemistry of organolead and organothallium compounds in the presence of microorganisms. *In* Organometals and Organometalloids. Occurrence and Fate in the Environment. F.E. Brinckman and J.M. Bellama (eds.). Am. Chem. Soc. Symp. Ser. No. 82. pp. 65-81.

Lee, A.G. 1971. The Chemistry of Thallium. Elsevier Publ. Co., Amsterdam, The Netherlands. 336 pp.

Magorian, T.R., K.G. Wood, J.G. Michalovic, S.L. Pek and M.M. Van Lier. 1974. Water Pollution by Thallium and Related Metals. Springfield, Virginia. NTIS PB 253 333. 182 pp. (Cited in U.S. EPA 1979.)

Mathis, B.J. and N.R. Kevern. 1975. Distribution of mercury, cadmium, lead and thallium in an eutrophic lake. Hydrobiologia 46: 207-222.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Thallium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 61.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1982. Data Sheets on Selected Toxic Elements. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 19252. pp. 43-45.

O'Shea, T.A. and K.H. Mancy. 1978. The effect of pH and hardness metal ions on the competitive interaction between trace metal ions and inorganic and organic complexing agents found in natural waters. Water Res. 12: 703-711.

Smith, I.C. and B.L. Carson. 1977. Trace Metals in the Environment. Vol. 1. Thallium. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 394 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. Department of the Interior. 1980. Thallium. *In* Mineral Facts and Problems. Bureau of Mines, Washington, D.C. pp. 931-932.

U.S. EPA. 1978. In-depth Studies in Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency, Washington, D.C. Contract No. 68-01-4646.

U.S. EPA. 1979. Thallium. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 18-1 to 18-8.

U.S. EPA. 1980. Ambient Water Quality Criteria for Thallium. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-074.

Zitko, V., W.V. Carson and W.G. Carson. 1975. Thallium: occurrence in the environment and toxicity to fish. Bull. Environ. Contam. Toxicol. 13: 23-30.

6.2.40 Tin (Inorganic)

6.2.40.1 Uses and Production

The properties of tin make it useful for the prevention of corrosion and other chemical reactions with various metals (McNeely *et al.* 1979). Tin foil is used for electrical condensers, bottle cap liners and food wrappings. Tin wire is used for fuses and safety plugs and in the production of plate glass. Tin plating over steel is the most important use of tin. Tin cans are the major tin products used in food packaging (Ontario Ministry of the Environment 1981). Tin alloys may be used in superconductive magnets (Ontario Ministry of the Environment

1981) or in pewter (McNeely *et al.* 1979). Tin is also used in numerous organic compounds, including biocides (see Section 6.3.10) (McNeely *et al.* 1979).

Canadian tin production is limited to minor by-product recovery by Cominco Ltd. at Kimberley, British Columbia. In 1984, 217 t of tin were produced at this plant. Rio Algom Ltd. plans to produce approximately 4500 t of tin annually at Yarmouth, Nova Scotia (Energy, Mines and Resources Canada 1985). Canadian tin consumption has been estimated at slightly less than 4500 t annually. In 1984, Canada imported 5409 t of tin and tin products (Bourassa 1985).

6.2.40.2 Sources and Pathways for Entering the Aquatic Environment

The concentration of tin in the earth's crust has been estimated at 2.0 mg·kg^{-1} (Weast 1983). In seawater, the estimated concentration is 0.8 μg·L^{-1} (McNeely *et al.* 1979). Tin is released by the weathering of igneous rocks that contain the mineral cassiterite or tinstone (SnO_2). The major anthropogenic sources of inorganic tin input to the environment are industrial discharges from mining, refineries, food processing and packaging plants, steel manufacture and construction. Municipal sewage can also be a source by discharging discarded household products containing tin to the aquatic environment (Ontario Ministry of the Environment 1981).

6.2.40.3 Environmental Concentrations

Tin is found in fresh water at very low concentrations. When detected, the concentrations range from 1 to 2 μg·L^{-1} (NAS 1977).

Inorganic tin concentrations were found to vary from 4 to 90 ng·L^{-1} (average 9 ng·L^{-1}) in fresh water (Bowen 1979). Lake Michigan fresh water contained 0.084-0.490 μg·L^{-1} (Hodge *et al.* 1979), whereas Ontario lakes and rivers contained inorganic tin in concentrations ranging from nondetectable to 50 μg·L^{-1} (Maguire *et al.* 1982). Inorganic tin concentrations in Canadian surface water microlayers varied from nondetectable to 633 μg·L^{-1} (Maguire *et al.* 1982). In comparison, Canadian freshwater sediments contained 0.08-5.13 mg·kg^{-1} (dry weight) (Maguire 1984).

Concentrations of tin in air of 0.003-0.3 μg·m^{-3} were found in samples taken from some industrial cities in the U.S.A. Dust from industrial regions of Europe is reported to contain concentrations of 10-10 000 mg·kg^{-1} (NAS 1977). No data on concentration ranges for inorganic tin in air in Canada are available.

6.2.40.4 Forms and Fate in the Aquatic Environment

Tin may occur in oxidation states of -4, 0, $+2$ and $+4$. In the aquatic environment, it will usually be found in the $+4$ oxidation state (Sn(IV)). Some divalent tin may occur in anaerobic sediments and in waters of low redox potential (Brinckman *et al.* 1983). The $+4$ oxidation state is thermodynamically more stable than the $+2$ state (Cotton and Wilkinson 1980); the half-life for the oxidation of Sn(II) to Sn(IV) in oxygenated water at 23°C has been reported to be 2 d (Fanchiang *et al.* 1978).

Tin(II) compounds, such as stannous chloride, are soluble in water; aqueous solutions, however, become turbid upon dilution because of oxidation and precipitation. Tin(IV) forms a large number of inorganic and organometallic compounds (see Section 6.3.10). The most likely forms of Sn(IV) in natural water include the hydroxides, $Sn(OH)_4$, and the hydroxyoxides, $SnO(OH)_2$ and $SnO(OH)_3^-$. In waters above pH 8 in the presence of dissolved oxygen, it has been suggested that $SnO(OH)_3^-$ is the dominant species (Stumm and Brauner 1975). The species $SnO(OH)_2$ is expected to dominate below pH 7 (Macchi and Pettine 1980).

There is little reliable information on the fate of inorganic tin in the aquatic environment. In general, tin concentrations increase as follows: water < surface microlayer < sediments (Bowen 1979; Maguire *et al.* 1982; Maguire 1984). Relatively few studies are available on the bioaccumulation of tin. Tin has been found in marine organisms (0.2-20 mg·kg^{-1}) (Bowen 1966). Fish from Ontario lakes and rivers contained inorganic tin at concentrations ranging from 0.17 to 0.3 mg·kg^{-1} for lake trout and averaging 0.62 mg·kg^{-1} (wet weight) for smelt, indicating the possibility for bioaccumulation (Chau *et al.* 1984).

Tin may be methylated in aqueous systems. Methyltin compounds may be formed from Sn(II) and Sn(IV) in the presence of *Pseudomonas* sp., isolated from estuarine sediments (Brinckman *et al.* 1983). Tin(IV) may be methylated in nutrient medium or natural water – sediment mixtures. Sediments from Canadian Shield lakes which were incubated in a microbiological medium containing tin were found to methylate tin (Chau *et al.* 1981). Dimethyltin and trimethyltin compounds were detected after 14 d of aerobic incubation in nutrient medium containing stannic chloride inoculated with sediment from Chesapeake Bay (Cooney *et al.* 1981; Hallas *et al.* 1982). Pure cultures of *Pseudomonas* were found to transform Sn(IV) and, to a lesser extent, Sn(II) to trimethyltin species (Jackson *et al.* 1982).

6.2.40.5 References

Bourassa, A. 1985. Tin. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 60.1-60.14.

Bowen, H.J.M. 1966. The determination of tin in biological material by using neutron-activation analysis. Analyst 97: 1003-1005.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Brinckman, F.E., J.A. Jackson, W.R. Blair, G.J. Olson and W.P. Iverson. 1983. Ultratrace speciation and biogenesis of methyltin transport species in estuarine waters. *In* Trace Metals in Sea Water (NATO Conf. Ser. 4: 9). C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (eds.). Plenum Press, New York. pp. 39-72.

Chau, Y.K., P.T.S. Wong, O. Kramer and G.A. Bengert. 1981. Methylation of tin in the aquatic environment. *In* Proc. 3rd Int. Conf. Heavy Metals in the Environment. Sept. 14-18, Amsterdam, The Netherlands. CEP Consultants Ltd., Edinburgh. pp. 641-644.

Chau, Y.K., R.J. Maguire, P.T.S. Wong, B.A. Glen, G.A. Bengert and R.J. Tkacz. 1984. Occurrence of Methyltin and Butyltin Species in Environmental Samples in Ontario. National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario. Natl. Water Res. Inst. Rep. No. 84-01. Unpublished report. 26 pp.

Cooney, J.J., L.E. Hallas and J.C. Means. 1981. Tin and microbes in the Chesapeake Bay, U.S.A. *In* Proc. 3rd. Int. Conf. Heavy Metals in the Environment. Sept. 14-18, Amsterdam, The Netherlands. CEP Consultants Ltd., Edinburgh. pp. 243-245.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, Toronto, Ontario. 1396 pp.

Energy, Mines and Resources Canada. 1985. Other nonferrous metals. Can. Min. J. 106(2): 60, 62.

Fanchiang, Y.-T., W.P. Ridley and J.M. Wood. 1978. Kinetic and mechanistic studies on B_{12}-dependent methyl transfer to certain toxic metal ions. *In* Organometals and Organometalloids. Occurrence and Fate in the Environment. F.E. Brinckman and J.M. Bellama (eds.). Am. Chem. Soc. Symp. Ser. 82: 54-64.

Hallas, L.E., J.C. Means and J.J. Cooney. 1982. Methylation of tin by estuarine microorganisms. Science 215: 1505-1507.

Hodge, V.F., S.L. Seidel and E.D. Goldberg. 1979. Determination of tin IV and organotin compounds in natural waters, coastal sediments and macro algae by atomic absorption spectrometry. Anal. Chem. 51: 1256-1259.

Jackson, J.A., W.R. Blair, F.E. Brinckman and W.P. Iverson. 1982. Gas-chromatographic speciation of methylstannanes in the Chesapeake Bay using purge and trap and sampling with a tin-selective detector. Environ. Sci. Technol. 16: 110-119.

Macchi, G. and M. Pettine. 1980. Voltametric characterization and chemical behaviour of inorganic tin in natural waters. Environ. Sci. Technol. 14: 815-818.

Maguire, R.J. 1984. Butyltin compounds and inorganic tin in sediments in Ontario. Environ. Sci. Technol. 18: 291-294.

Maguire, R.J., Y.K. Chau, G.A. Bengert, E.J. Hale, P.T.S. Wong and O. Kramer. 1982. Occurrence of organic compounds in Ontario lakes and rivers. Environ. Sci. Technol. 16: 698-702.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Tin. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 61.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

Ontario Ministry of the Environment. 1981. Outlines of Analytical Methods: a Guide to the Occurrence, Significance, Sampling and Analysis of Chemical and Microbiological Parameters in Water, Sediment, Soil, Vegetation and Air. Coordinated by Water Quality Section, Laboratory Services Branch, Toronto, Ontario. 280 pp.

Stumm, W. and P.A. Brauner. 1975. Chemical speciation. *In* Chemical Oceanography. 2nd edition. J.P. Riley and G. Skirrow (eds.). Academic Press, New York. pp. 173-239.

Weast, R.C. (ed.). 1983. Handbook of Chemistry and Physics. 64th edition. Chemical Rubber Co. Press, Cleveland, Ohio.

6.2.41 Titanium

6.2.41.1 Uses and Production

Titanium metal is extensively used in the aircraft industry. Because of its resistance to corrosion and its inertness, titanium is used in the chemical, metallurgical and paper industries, in power plants and in desalination plants. Titanium dioxide (TiO_2) is the most extensively used titanium compound; it is used as a white pigment in paints, lacquers, enamels, paper coatings and plastics. It is also used as a colour additive in confections, dairy products and bread flour. Titanium tetrachloride ($TiCl_4$) is used as an intermediate in the production of titanium metal and pigments and as a component and catalyst in the chemical industry. Titanous chloride ($TiCl_3$) is used as a colouring agent and as a polymerization catalyst. Titanium metal is also used to fabricate surgical and prosthetic devices. Organotitanium compounds are used as catalysts for polymerization processes, as water repellants and in dyes (Friberg *et al*. 1979; U.S. Department of the Interior 1980; King 1985).

Canadian manufacture and mining of titanium occur only in the Province of Quebec (King 1985). Information on production, importation, consumption and exportation of titanium dioxide is presented in Table 6-57. Canada does not produce primary titanium or ferrotitanium of the quality required to satisfy aircraft specifications. Importation and exportation of titanium metal and other titanium compounds (excluding titanium dioxide) are presented in Table 6-58. One of the most important ores containing titanium is ilmenite. Canada ranks second (16%) in the world for ilmenite concentrate production. In 1983, Canada produced 612 000 t of ilmenite concentrate, and world production was 3 755 000 t (King 1985).

Table 6-57. Production, Consumption, Importation and Exportation of Titanium Dioxide in Canada

	Amount (t)	
Parameter	1983	1984
Production	75×10^3	78×10^3
Consumption	63×10^3	68.3×10^3
Importation	14.6×10^3	17×10^3
	18.5×10^3 [1]	21×10^3 [1]
Exportation	23×10^3	26.5×10^3

[1] King 1985.

Source: CORPUS Information Services 1984.

Table 6-58. Importation and Exportation of Titanium Metal and Other Titanium Compounds in Canada[1]

	Importation (t)		Exportation (t)	
Compound	1983	1984	1983	1984
Titanium metal	275	284	415[2]	5[2]
			287[3]	150[3]
Ferrotitanium (total alloy weight)	14	10	NA[4]	NA

[1] Excluding titanium dioxide (see Table 6-57).

[2] Unwrought, including waste and scrap.

[3] Wrought.

[4] NA = not available.

Source: King 1985.

6.2.41.2 Sources and Pathways for Entering the Aquatic Environment

Titanium ranks eighth in order of abundance in igneous rocks; it is estimated to constitute 0.43% of the earth's crust. The most important ores of titanium are ilmenite ($FeTiO_3$) and rutile (TiO_2). Titanium is also found as a silicate (sphene), as calcium titanate ($CaTiO_3$) and in association with hematite deposits (NAS 1980).

Titanium may reach the aquatic environment in effluents from mining, smelting and manufacturing (i.e. of pigments) of the metal and its compounds. Leaching from the titania slag produced from the smelting of ilmenite ore can introduce titanium to surface waters and groundwaters. Municipal effluents may contain titanium through discarded products containing titanium as a pigment or coating (King 1985).

Information on concentrations of titanium in industrial or municipal effluents is limited. The final effluents of five organic chemical plants in Canada contained titanium above the detection limit (0.002 $\mu g \cdot L^{-1}$). The concentration range reported was 0.003-0.596 $mg \cdot L^{-1}$ based on five samples taken from four plants in February and March of 1985. A fifth plant reported a combined effluent concentration of 1.27 $mg \cdot L^{-1}$ (Sigma Resource Consultants Ltd.).

6.2.41.3 Environmental Concentrations

Titanium concentrations of 2-107 $\mu g \cdot L^{-1}$ have been found in fresh water in Canada and the U.S.A. (Friberg *et al.* 1979). Sampling results for titanium are not reported in NAQUADAT (1985). Drinking water in the U.S.A. was found to contain titanium ranging in concentration from 0.5 to 15 $\mu g \cdot L^{-1}$. Titanium concentrations in seawater are in the 0.6-1 $\mu g \cdot L^{-1}$ range (Friberg *et al.* 1979).

Atmospheric concentrations for titanium in Canada are unavailable, but U.S. data estimate an average concentration below 0.1 $\mu g \cdot m^{-3}$ in urban areas (Friberg *et al.* 1979).

6.2.41.4 Forms and Fate in the Aquatic Environment

Titanium occurs in oxidation states of -1, 0, $+2$, $+3$ and $+4$, with tetravalent titanium (Ti(IV)) being the stable and common oxidation state. Compounds in lower oxidation states are quite readily oxidized to Ti(IV). The simple aquated tetravalent ion does not exist in aqueous solution, and titanic (Ti(IV)) compounds are usually covalent. Tetravalent titanium compounds, such as titanium halides, readily hydrolyze in water to species containing the Ti–O bond, primarily hydrated oxides such as TiO_2. In aqueous solutions at pH values typically encountered in natural waters, titanium would be present as colloidal or precipitated hydrous TiO_2. In strongly alkaline solutions, some titanates (TiO_3^{2-}) would be formed (Cotton and Wilkinson 1980; Windholtz *et al.* 1983).

Titanium is not considered to be an essential element for either plants or animals (NAS 1980). Titanium is accumulated in hard siliceous tissues, and is present in terrestrial plants (1.5-56 $mg \cdot kg^{-1}$), edible vegetables (<0.02-3 $mg \cdot kg^{-1}$), mammalian muscle (1-2 $mg \cdot kg^{-1}$) and marine algae (3-40 $mg \cdot kg^{-1}$) and fish (0.2 $mg \cdot kg^{-1}$). In comparison, the concentrations in fresh water and seawater average 5 and 1 $\mu g \cdot L^{-1}$, respectively (Bowen 1979).

6.2.41.5 References

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

CORPUS Information Services. 1984. Titanium dioxide. CPI Product Profiles. Don Mills, Ontario.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, Toronto, Ontario. 1396 pp.

Friberg, L., Nordberg, G.F. and V.B. Vouk (eds.). 1979. Titanium. *In* Handbook on the Toxicology of Metals. Chap. 38. Elsevier/North-Holland Biomedical Press, New York.

King, D.E.C. 1985. Titanium and titanium dioxide. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 61.1-61.9.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1980. Mineral Tolerance of Domestic Animals. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

U.S. Department of the Interior. 1980. Titanium. *In* Mineral Facts and Problems. Bureau of Mines, Washington, D.C.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

Table 6-59. Production, Consumption and Importation of Tungsten in Canada

Parameter	Compound	Amount (t)		
		1981	1982	1983
Production	Tungsten trioxide	2515	3030	1538
Consumption	Tungsten content	402	508	NA[1]
Importation	Tungsten ore	14	7.6	12
	Ferrotungsten	6	4.5	3
	Tungsten carbide powder	NA	274	220
	Tungsten carbide rotary rock	NA	10.2	9.75
	Tungsten carbide percussion	NA	89.2	185.4

[1] NA = not available.

Source: Phillips 1985.

6.2.42 Tungsten

6.2.42.1 Uses and Production

Tungsten's physical and chemical properties make it suitable for many commercial and industrial applications. Tungsten and its alloys are widely used as filament materials in incandescent lamps and as components of high-temperature structural products where hardness and strength are needed. Tungsten carbide (W_2C) is used in the metalworking, mining and petroleum industries (Cotton and Wilkinson 1980). Calcium and magnesium tungstates are used in fluorescent lighting, and other salts of tungsten are used in the chemical and tanning industries (McNeely *et al.* 1979).

Production, consumption and importation of tungsten in Canada are presented in Table 6-59. World production of tungsten ores and concentrates was 44 328 and 38 320 t in 1982 and 1983, respectively. Canada is the fifth largest producer of tungsten ores and concentrates in the world (Phillips 1985).

6.2.42.2 Sources and Pathways for Entering the Aquatic Environment

Tungsten is found almost exclusively in the forms of tungstates, the chief minerals being wolframite ((Fe, Mn)WO_4), scheelite ($CaWO_4$) and stolzite ($PbWO_4$). Commercially, tungsten is obtained from the tungstate ores by reducing tungstic oxide to the metal (Cotton and Wilkinson 1980).

6.2.42.3 Environmental Concentrations

Most fresh waters contain negligible concentrations of tungsten. Concentrations of tungsten in fresh water and seawater average 0.03 and 0.1 $\mu g \cdot L^{-1}$, respectively (Bowen 1979). The Western and Pacific regions reported environmental concentrations for tungsten below the detection limit (10 $mg \cdot L^{-1}$, extractable) based on 45 and 53 samples, respectively, taken prior to 1980 (NAQUADAT 1985).

6.2.42.4 Forms and Fate in the Aquatic Environment

Tungsten, a transition metal which is chemically similar to chromium, molybdenum and tantalum, occurs in oxidation states of +2, +3, +4, +5 and +6. Numerous tungsten oxides are known; the trioxides dissolve in alkaline solution to yield tungstate (WO_4^{2-}) solutions. Tungstate is not a strong reducing agent, unlike chromate. Alkali metal, ammonium, magnesium and thallous salts of tungsten are soluble in water, whereas tungsten salts of other metals are nearly all insoluble (Cotton and Wilkinson 1980; Windholtz *et al.* 1983).

6.2.42.5 References

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, London. 333 pp.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. A Comprehensive Text. 4th edition. John Wiley & Sons, New York. 1396 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Tungsten. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 62.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Phillips, D.R. 1985. Tungsten. *In* Canadian Minerals Yearbook 1983-1984. Review and Outlook. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. pp. 62.1-62.8.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

6.2.43 Uranium

6.2.43.1 Uses and Production

Uranium is used as a nuclear fuel by nuclear-powered electrical generating stations (Berlin and Rudell 1979; Environment Canada 1983). Other uses include internal guidance devices for missiles, radio emissions shielding material and photographic emulsions. Porcelains used in dentistry, optical lenses and alloys may contain uranium, and certain uranium compounds are used as catalysts in the chemical industry (Berlin and Rudell 1979; Harmsen and de Haan 1980; Health and Welfare Canada 1980). Other uses of uranium involve its radiological nature, where it is used in minute quantities as a radioactive tracer (Environment Canada 1983). Depleted uranium, a waste product from nuclear reprocessing and uranium enrichment, may be used to prepare alloys to be further processed in special steel making (Environment Canada 1983).

Uranium is mined in 15 countries (Berlin and Rudell 1979; Energy, Mines and Resources Canada 1981). Uranium ores containing as little as 0.1% and as much as 60% uranium are mined commercially (Berlin and Rudell 1979). Values ranging from 0.05 to 1% for medium-grade ores occur frequently in the U.S.A., whereas a 1-4% range (high-grade ore) is characteristic for Canada and Zaire. Recovery of uranium from ores commonly exceeds 90%, and is achieved by leaching ores and extraction of the uranium from the leach solution by ion exchange, solvent extraction or direct precipitation (Environment Canada 1983).

Uranium ores in Canada are found mainly in Ontario, northern Saskatchewan, Northwest Territories, Quebec and New Brunswick. Minor deposits are located in British Columbia and Labrador (Energy, Mines and Resources Canada 1981; Whillans 1983). Major deposits are also found in northern Australia, South Africa, the United States, U.S.S.R., China and Brazil (Energy, Mines and Resources Canada 1981).

Canada's production of uranium (estimated as elemental U) in 1984 was 9693 t, of which 45% was produced in Ontario and 54% in Saskatchewan (Energy, Mines and Resources Canada 1985). Approximately 15% of Canadian production remains in Canada; the rest is exported (Energy, Mines and Resources Canada 1981). In 1982, Canada imported 171 t of uranium (Statistics Canada 1983). World demand for uranium by the year 1995 is estimated to be about 70 000 t (Energy, Mines and Resources Canada 1981).

6.2.43.2 Sources and Pathways for Entering the Aquatic Environment

Uranium is found in greatest quantities in acidic igneous rocks and in smaller quantities in sedimentary and basic igneous rocks. It occurs in numerous minerals, such as uraninite (UO_2), carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$], autunite [$Ca(UO_2)_2\ (PO_4)_2 \cdot 10\text{-}12H_2O$] and tobernite [$Cu(UO_2)_2\text{-}(PO_4)_2 \cdot 8\text{-}12H_2O$] (McNeely *et al.* 1979).

Most uranium occurs as a mixture of the three common isotopes, with ^{238}U, ^{235}U and ^{234}U contributing ~99.25, ~0.71 and ~0.0075%, respectively (Environment Canada 1983). The abundance of uranium in the earth's crust is relatively low, ranging from 2.7×10^{-4} to $4.0 \times 10^{-4}\%$ (Riley and Chester 1971; Berlin and Rudell 1979). The total amount of uranium in the earth's crust to a depth of 20 km has been estimated to be 1×10^{14} t (Health and Welfare Canada 1980).

Geologically, uranium is a very mobile element. The approximate amounts of uranium mobilized from rock by weathering and natural erosion can be calculated from the weathering rates of the various rock types and their average uranium concentrations. The calculated results, indicated in Table 6-60, reveal that approximately 27 275-32 325 t of uranium are moved worldwide each year (Eriksson 1960; Bowen 1966; Environment Canada 1983). Uranium additions to the world's oceans by river flows and sediments are about 11 000 and 8000 $t \cdot a^{-1}$, respectively (Goldberg 1976).

Weathering of uranium is a process wherein the element, mostly in the mineral form of uraninite, undergoes oxidative dissolution to the soluble uranyl ion (UO_2^{2+}) by the action of surface waters and groundwaters (Environment Canada 1983). Rates of dissolution of uraninite (U(IV)) are dependent on the dissolved oxygen content of the water, total dissolved carbonate, temperature, pH, Eh, organic content and concentrations of other dissolved substances (Taylor 1979).

Wastes from uranium mines and nuclear fuel processing plants may contribute uranyl ions to water. The combustion of organic (wood, peat) and fossil fuels and the roasting of rock minerals in the metal extraction and refining and cement industries, as well as the incineration of solid wastes, can be significant anthropogenic pathways for uranium entry into the

Table 6-60. Estimated Uranium Released to the Environment Globally as a Result of Weathering and Erosion[1]

Type of rock	Weathering rate (10^6 t·a^{-1})	Average concentration (mg·kg^{-1})	Total U released (t·a^{-1})
Igneous	700-1500	2.7	1890-4050
Shale	6500	3.7	24 050
Sandstone	1500	0.45	675
Limestone	300	2.2	660
Total	9000-9800		27 275-32 325

[1] Cited in Environment Canada 1983.

Sources: Eriksson 1960; Bowen 1966.

atmospheric environment. Uranium from these sources eventually finds its way to surface waters (Environment Canada 1983).

6.2.43.3 Environmental Concentrations

Uranium is widely distributed in the earth's crust, with an average concentration of about 3-4 μg·g^{-1} (Statistics Canada 1983).

In Canada, the uranium concentrations in inland surface waters from the Rocky Mountain cordillera streams range from 0.02 to 89.8 μg·L^{-1}, with the median value of 22 580 samples being 0.1 μg·L^{-1} (Garrett 1982). Waters from approximately 37 000 Canadian Shield lakes (Labrador, Ontario, Manitoba, Saskatchewan, the Northwest Territories and Baffin Island, sampled between 1976 and 1978) ranged in concentration from 0.001 to 170.0 μg·L^{-1}, with a median value of 0.05 μg·L^{-1} (Environment Canada 1983). Lake Michigan water has a uranium concentration of 0.2 μg·L^{-1} (Wahlgren and Orlandini 1982). Lake Ontario water near Port Hope, Ontario, which is taken for public water supplies, has a uranium concentration of about 1.1 μg·L^{-1} (IJC 1981). Uranium concentrations for various Canadian regions are presented in Table 6-61. Freshwater stream sediments of the Rocky Mountains have a median value of 3.4 mg·kg^{-1} (23 501 samples). Uranium levels in the Canadian Shield lake sediments range from 0.1 to 733 mg·kg^{-1}, with a median value of 4.6 mg·kg^{-1} (41 028 samples) (Garrett 1982). Whole lake mean concentrations of uranium in the sediments in the Great Lakes are presented in Table 6-62.

Groundwater has varying concentrations of uranium. The average uranium concentration for groundwater in Canada is 0.2 μg·L^{-1} (Health and Welfare Canada 1980). Some areas may, however, have higher concentrations. For example, some isolated water wells in the Tweed area of southeastern Ontario have uranium concentrations as high as 80 μg·L^{-1} (Environment Canada 1983). Mean concentrations of uranium in wells in southwestern Saskatchewan varied from a low of 0.8 μg·L^{-1} to a high of 39 μg·L^{-1} (Dyck *et al.* 1976). Studies conducted in the United States, Europe and Australia found that most concentrations are less than 2.2 μg·L^{-1} (Harmsen and de Haan 1980).

Canadian environmental concentration ranges for uranium, obtained from NAQUADAT, are presented in Table 6-63.

Table 6-61. Concentrations of Uranium in Water, Sediments, Soils and Rocks in Various Regions of Canada

Location	Concentration[1] of uranium	Sample media
Newfoundland	1.47-2.38 mg·kg^{-1}	Lake sediment
	15-155 ng·L^{-1}	Lake water
Ontario	5.08-5.35 mg·kg^{-1}	Lake sediment
	65-115 ng·L^{-1}	Lake water
Saskatchewan	3.34-6.15 mg·kg^{-1}	Lake sediment
	7.00[2] mg·kg^{-1}	Stream sediment (contaminated)
	5.10[2] mg·kg^{-1}	Stream sediment (uncontaminated)
	21 ng·L^{-1}	Lake water
British Columbia	8.99-13.7 mg·kg^{-1}	Stream sediment
	190-273 ng·L^{-1}	Stream water
Northwest Territories	22.0-24.7 mg·kg^{-1}	Lake sediment
	132-154 ng·L^{-1}	Lake water
Yukon	3.04-12.00 mg·kg^{-1}	Stream sediment
New Brunswick, Nova Scotia, Prince Edward Island	1000 ng·L^{-1}	Well water

[1] Values are arithmetic means unless specified otherwise.

[2] Geometric mean.

Source: NRCC 1983.

Table 6-62. Mean Concentrations of Uranium in Great Lakes Sediments (Whole Lake)

Lake	Mean concentration (mg·kg^{-1})	Range[1] (mg·kg^{-1})	Standard deviation
Superior	0.59	≤0.2-1.9	0.4
Huron	0.41	≤0.2-1.5	0.27
Georgian Bay	0.38	≤0.2-1.7	0.27
Michigan	2.19	0.5-9.2	1.05
St. Clair (1970)	1.16	≤0.2-2.0	0.56
(1974)	1.22	0.4-2.5	0.58
Erie	0.43	≤0.2-2.8	0.33
Ontario	0.23	≤0.2-0.9	0.10

[1] Minimum detection limit is 0.2 mg·kg^{-1}.

Sources: Thomas 1982; Environment Canada 1983.

Table 6-63. Environmental Concentration Ranges for Uranium in Canadian Surface Waters

Region	Concentration range[1] (dissolved) (μg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.10-2.10	19	Prior to 1980
Western (3 stations)	0.097-2.14	7	1980-1983
Central[2] (streams/rivers)	0.28-0.65	14	1981-1982
Atlantic	0.25-0.73	9	1981-1983

[1] Detection limit is 0.1 μg·L^{-1}.

[2] Only Ontario samples were reported.

Source: NAQUADAT 1985.

6.2.43.4 Forms and Fate in the Aquatic Environment

Uranium may exist in oxidation states of +3, +4, +5 and +6, with the hexavalent state being the most stable. Uranium in elemental form does not occur naturally because it is a very reactive reducing metal. The aqueous chemistry of the hexavalent ion is that of the dioxo ion, UO_2^{2+} (uranyl ion), which is quite stable; it forms stable salts and complexes with many commonly occurring anions. Generally, in oxidizing environments, the uranyl (U(VI)) ion predominates, whereas the uranous (U(IV)) ion is present in reducing environments. The chemical speciation of uranium ions in aqueous solution is quite complex because of the many possibilities of complexing reactions with all ions, other than ClO_4^-. Hydrolytic reactions may also lead to polymeric ions. Uranium may be precipitated as insoluble UO_2 or be adsorbed by clays and hydrous metal oxides (Cotton and Wilkinson 1980).

In aerobic waters, the most significant complexing agent for uranium is carbonate. Below pH 5, the predominant uranium species are UO_2^{2+} and UO_2OH^+; however, above pH 5 and in the presence of carbon dioxide, carbonate species predominate. At pH 5, the dominant form of uranium is neutral UO_2CO_3; at pH 6-7, $UO_2(CO_3)_2^{2-}$ dominates; and at pH 8, $UO_2(CO_3)_3^{4-}$ dominates. These uranyl carbonate species are all quite stable in the typical ranges of redox potential found in natural waters. Sulphur complexes are also soluble, whereas potassium and phosphate complexes are quite insoluble (Taylor 1979; Giblin *et al*. 1981).

Sorption plays a dominant role in determining the fate of uranium in the aquatic environment. Sorption to clay minerals such as kaolinite below pH 5 and sorption to hydrous ferric oxide at higher pH in aerobic waters will reduce the mobility of uranium (Giblin *et al*. 1981).

Uranium is not an essential element; however, it is found in most living tissues (Bowen 1979). It may be accumulated by numerous aquatic plants, lower organisms, invertebrates and fish (Environment Canada 1983). It is taken up from water by the alga *Ochromonas* sp. and concentrated by a factor of 330 in 48 h (Morgan 1961) and by the green alga *Spirogyra* sp. by a factor of 2096 (Stegner and Kobal 1982). Uranium reached extracellular concentrations of 10-15% of dry cell weight in the yeast *Saccharomyces cerevisiae*, with optimal sorption occurring at pH 5.9-6.8 (Strandberg *et al*. 1981). High concentrations of uranium were found in the benthic invertebrates Trichoptera (2.88 $mg \cdot kg^{-1}$ (dry weight)) and *Gammarus fossarum* (0.06 $mg \cdot kg^{-1}$ (dry weight)) taken from a stream polluted with uranium mine water (Stegner and Kobal 1982). Zooplankton from Lake Superior, Lake Michigan and Lake Erie had uranium concentrations of approximately 18 $\mu g \cdot kg^{-1}$. In comparison, the average uranium concentration of small whole forage fish (*Alosa pseudoharengus*, *Notropis hudsonius*, *Percopsis omiscomaycus*) was 3 $\mu g \cdot kg^{-1}$ (dry weight). The average concentration of uranium found in the livers of fish representing Salmoidae, Coregonidae, Percidae, Cyprinidae, Osmeridae and Perciformes was approximately 2 $\mu g \cdot kg^{-1}$ (dry weight) (Lucas *et al*. 1970). Lake trout (*Salvelinus namaycush*) and cisco (*Coregonus artedii*) sampled from waters of the Northwest Territories during a study on mine wastes and receiving waters had muscle burdens of 190-290 and 110 $\mu g \cdot kg^{-1}$, respectively. Livers contained 120-180 and 120 $\mu g \cdot kg^{-1}$, respectively (Falk *et al*. 1973). Because uranium concentrations decrease with increasing trophic status, biomagnification is not expected (Lucas *et al*. 1970).

6.2.43.5 References

Berlin, M. and B. Rudell. 1979. Uranium. *In* Handbook on the Toxicology of Metals. L. Friberg, G.F. Nordberg and V.B. Vouk (eds.). Elsevier/North-Holland Biomedical Press, Amsterdam, The Netherlands. (Cited in Environment Canada 1983.)

Bowen, H.J.M. 1966. Trace Elements in Biochemistry. Academic Press, London. (Cited in Environment Canada 1983.)

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press, Toronto, Ontario. 333 pp.

Cotton, F.A. and G. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, Toronto. 1396 pp.

Dyck, W., R.A. Campbell and S.H. Whitaker. 1976. Well water uranium reconnaissance, southwestern Saskatchewan. *In* Uranium in Saskatchewan. Spec. Publ. Sask. Geol. Soc. Vol. 3. pp. 157-168.

Energy, Mines and Resources Canada. 1981. Uranium in Canada 1980. Assessment of Supply and Requirements. Report EP 81-3.

Energy, Mines and Resources Canada. 1985. Canadian mineral production 1983 and 1984. Can. Min. J. 106(2): 26-27.

Environment Canada. 1983. Uranium. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Eriksson, E. 1960. The yearly circulation of chloride and sulfur in nature; meteorological, geochemical and pedological implications. Tellus 12: 63-109. (Cited in Environment Canada 1983.)

Falk, M.R., M.D. Miller and S.J.M. Kostiuk. 1973. Biological Effects of Mining Wastes in the Northwest Territories. Canadian Fisheries and Marine Service (CEN/T-73-10). (Cited in Environment Canada 1983.)

Garrett, R.G. 1982. Personal communication. Geological Survey of Canada, Ottawa. (Cited in Environment Canada 1983.)

Giblin, A.M., B.D. Batts and D.J. Swaine. 1981. Laboratory simulation studies of uranium mobility in natural waters. Geochim. Cosmochim. Acta 45: 699-709.

Goldberg, E.D. 1976. The Health of the Oceans. UNESCO Press, Paris. pp. 97-117. (Cited in Environment Canada 1983.)

Harmsen, K. and F.A.M. de Haan. 1980. Occurrence and behaviour of uranium and thorium in soil and water. Neth. J. Agric. Sci. 28: 40-62. (Cited in Environment Canada 1983.)

Health and Welfare Canada. 1980. Uranium. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 677-690.

IJC. 1981. Report on Great Lakes Water Quality. Appendix Report by the Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

Lucas, H.F., Jr., D.N. Edgington and P.J. Colby. 1970. Concentrations of trace elements in Great Lakes fishes. J. Fish. Res. Board Can. 27: 677-684.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Uranium. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 63-64.

Morgan, G.B. 1961. The adsorption of radioisotopes by certain microorganisms. Q. J. Fl. Acad. Sci. 24: 94-100.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1983. Radioactivity in the Canadian Aquatic Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 19250. 290 pp.

Riley, J.P. and R. Chester. 1971. Introduction to Marine Chemistry. Academic Press, New York. (Cited in Environment Canada 1983.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Stegnar, P. and I. Kobal. 1982. Uptake and distribution of radium and uranium in the aquatic food chain. *In* Proc. Int. Symp. on Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle. July 1981, Knoxville, Tennessee. (Cited in Environment Canada 1983.)

Strandberg, G.W., S.E. Shumate, II and J.R. Parrot, Jr. 1981. Microbial cells as biosorbents for heavy metals: accumulation of uranium by *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*. Appl. Environ. Microbiol. 41: 237-245.

Taylor, G.H. 1979. Biogeochemistry of uranium minerals. *In* Biogeochemical Cycling of Mineral-forming Elements. P.A. Trudinger and D.J. Swaine (eds.). Stud. Environ. Sci. Vol. 3. Elsevier Scientific Publ. Co., New York. pp. 485-514.

Thomas, R. 1982. Personal communication. Great Lakes Biolimnology Laboratory, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario. (Cited in Environment Canada 1983.)

Wahlgren, M.A. and K.A. Orlandini. 1982. Comparison of the geochemical behaviour of plutonium, thorium and uranium in selected North American lakes. *In* Proc. Int. Symp. on Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle. July 1981, Knoxville, Tennessee. (Cited in Environment Canada 1983.)

Whillans, R.T. 1983. Uranium. *In* Canadian Minerals Yearbook 1980. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa.

6.2.44 Vanadium

6.2.44.1 Uses and Production

Vanadium and its compounds are used in metallurgy (steel for use in combustion, tools and dies and springs, high-strength titanium alloys), as catalysts in the production of polymeric plastics, sulphuric and nitric acids and in dyes, inks and paints (Venugopal and Luckey 1978).

Vanadium is found in both crude oil and coal (NAS 1974). The average vanadium content in western Canadian and Venezuelan crude oils is 43 and 112 mg·kg^{-1}, respectively (Bertine and Goldberg 1971; NAS 1974). In the United States, coal has an average vanadium content of 25 mg·kg^{-1} (Bertine and Goldberg 1971; Zoller *et al.* 1973; NAS 1974).

Vanadium is used at levels of 0.05-5% in a wide variety of steel products (NAS 1974). The steel industry accounts for more than 90% of total vanadium consumption in the form of standard ferrovanadium or other vanadium ferroalloys (Shaw 1984).

Vanadium, in the form of V_2O_5, is not currently produced in Canada. Masterloy Products Ltd., however, imports V_2O_5 for the production of ferrovanadium at its Ottawa plant. Canada imported 562 t of ferrovanadium in 1981. Canadian consumption of ferrovanadium was 674 t in 1981 (Shaw 1984).

6.2.44.2 Sources and Pathways for Entering the Aquatic Environment

Vanadium is a ubiquitous element in the earth's crust, being 22nd in abundance, and is associated with basic igneous rock, carbonatite complexes, titaniferous magnetite complexes and chromite, uranium, iron and manganese deposits (Rose 1973). Ores with high vanadium content include partonite, roscoelite, vanadinite, descloizite, phosphate rock and carnotite (Shamberger 1978; Shaw 1984). Vanadium is present in coal and crude oil (NAS 1974). Natural seepage from carbonaceous deposits (e.g. oil sands) constitutes one source of vanadium input to the aquatic environment (van Zinderen Bakker and Jaworski 1980).

Vanadium enters the aquatic environment by various means, such as atmospheric deposition, weathering of vanadium-enriched ores, clays and slags and the leaching of coal-mining waste dumps and coal ash (Zoller *et al.* 1973; van Zinderen Bakker and Jaworski 1980). Vanadium may bind to naturally occurring organic complexing agents, adsorb on anion exchangers (clay particles) or coprecipitate with and adsorb on hydrous, amorphous ferric oxide in soil (Hopkins *et al.* 1977).

By far the greatest amount of vanadium is released by surface erosion (van Zinderen Bakker and Jaworski 1980). It is estimated that water dissolves and transports 32×10^3 t of vanadium to the oceans via rivers, and an additional 280×10^3 t are transported in particulates and suspended solids (Bertine and Goldberg 1971; Shamberger 1978). The anthropogenic contribution to water and sediments is far smaller than the total natural release of vanadium (Schroeder 1970, 1974; Bertine and Goldberg 1971).

Vanadium mobilization resulting from man's activities is mainly in the form of airborne particles derived from oil and coal combustion and, on a smaller scale, steel production (van Zinderen Bakker and Jaworski 1980). The average concentration of atmospheric vanadium over nonurban areas of the United States ranges from less than 1 to 40 ng·m^{-3} (NAS 1974).

The total airborne emissions of vanadium in Canada via steel production resulted in only a 1% contribution to total atmospheric loading (Environment Canada 1976). Peak vanadium concentrations in the air of Canadian cities may reach 10 000-20 000 ng·m^{-3} if vanadium-rich fuel oils are used (van Zinderen Bakker and Jaworski 1980). The use of such oil is prevalent in Atlantic regions (NAS 1974). High emission rates have been reported for all provinces east of Ontario, with Quebec accounting for 64% of the Canadian total (Environment Canada 1976).

6.2.44.3 Environmental Concentrations

Vanadium concentrations in fresh water range from below 0.3 to 200 μg·L^{-1} (Schroeder 1970; NAS 1974). Vanadium concentrations of 0-0.1 μg·L^{-1} were found in Lake Ontario (Chau *et al.* 1970). The Pacific region was sampled once (prior to 1980) for vanadium (total) and the value 900 μg·L^{-1} (detection limit 0.5 μg·L^{-1}) was obtained (NAQUADAT 1985).

The Western region reported a vanadium (total) concentration range of nondetectable (0.5 μg·L^{-1}) to 19 μg·L^{-1} based on 183 samples taken between 1980 and 1985. The Western region also reported a vanadium (recoverable) concentration range of nondetectable (1 μg·L^{-1}) to 0.11 mg·L^{-1} based on 1763 samples taken between 1980 and 1985 (NAQUADAT 1985). Groundwater concentrations of vanadium, usually in the soluble pentavalent forms, have been reported to be less than 1 μg·L^{-1} (NAS 1974; Strosher and Peake 1976). Municipal water may contain 1-6 μg·L^{-1} (Beliles 1978).

6.2.44.4 Forms and Fate in the Aquatic Environment

Vanadium, having oxidation states of 0, +1, +2, +3, +4 and +5, occurs in nature in oxidized form as metal vanadates. Vanadium compounds in the bi- and tri-oxidation states are basic, whereas those in the tetra- and penta-oxidation states are amphoteric (Shamberger 1978). Generally, vanadium is present in the earth's crust as a relatively insoluble salt in the trivalent form. Only in certain rare sulphide minerals does vanadium occur in the bivalent form in nature (Rose 1973).

Vanadium is highly mobile in neutral or alkaline environments. Its mobility decreases in oxidizing and acidic environments, whereas in reducing environments it is nearly immobile (Brooks 1972). Vanadium can oxidize to the pentavalent form from the tetravalent form (actually a mixture of VO_4^{3}, $V_2O_7^{4-}$, $V_4O_{11}^{2-}$ and $V_6O_{16}^{3-}$) and become soluble in water (Rose 1973; Shamberger 1978). Dissolved vanadium is usually in the pentavalent form. Vanadium pentoxide has a water solubility of 7 $mg \cdot L^{-1}$ (NAS 1974).

Although vanadium speciation has been studied extensively in marine systems, studies of vanadium speciation in freshwater systems are scarce (Allan and Brunskill 1976; Kemp *et al.* 1976; Allan and Jackson 1978). The vanadium species usually found in groundwater from the Athabaska oil sands are in the pentavalent form (Schroeder 1970; NAS 1974). In England, Ireland, Japan, Sweden and the United States, vanadium was found to be a constituent of hard water, but was absent from soft water (Shamberger 1978). Most of the vanadium in rivers reaching the sea precipitates, thereby enriching the marine muds (Schroeder 1970; NAS 1974).

Little information is available on the bioaccumulation of vanadium by freshwater species, although some marine benthic invertebrates, particularly tunicates, accumulate vanadium to levels 10^5-10^6 times those found in normal marine environments (Biggs and Swinehart 1976). Some marine algae have been found to accumulate vanadium. Uptake also occurs in higher plants, with elevated vanadium concentrations in *Pontedaria cordata*, *Phyllospadix iwatensis* and *Thalassia testudinum* (Lee 1983). Trace quantities of vanadium have been found in freshwater and marine fish. Studies on the extent of vanadium bioaccumulation in aquatic ecosystems show little evidence for biomagnification (Lee 1983).

6.2.44.5 References

Allan, R.J. and G.J. Brunskill. 1976. Relative atomic variation (RAV) of elements in lake sediments: Lake Winnipeg and other Canadian lakes. *In* Interactions Between Sediments and Freshwater. G.L. Golterman (ed.). Junie and Pudoc, The Hague. pp. 108-120.

Allan, R. and T. Jackson. 1978. Heavy Metals in Bottom Sediments of the Mainstream Athabasca River System in the AOSERP Study Area. AOSERP (Alberta Oil Sands Environmental Research Program) Report No. 34. Edmonton, Alberta. 72 pp. (Cited in van Zinderen Bakker and Jaworski 1980.)

Beliles, R.P. 1978. The lesser metals. *In* Toxicity of Heavy Metals in the Environment. Part 2. F.W. Oehme (ed.). Marcel Dekker Inc., New York. pp. 547-615. (Cited in van Zinderen Bakker and Jaworski 1980.)

Bertine, K.K. and E.D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233-235.

Biggs, W.R and J.H. Swinehart. 1976. Metal ions in biological systems. *In* Vanadium in Selected Biological Systems. H. Sigel (ed.). Marcel Dekker Inc., New York. pp. 141-196. (Cited in van Zinderen Bakker and Jaworski 1980.)

Brooks, R.R. 1972. Geobotany and Biogeochemistry of Mineral Exploration. Harper and Row Publ., New York. 290 pp. (Cited in van Zinderen Bakker and Jaworski 1980.)

Chau, Y.K., V.K. Chawla, H.F. Nicholson and R.A. Vollenweider. 1970. Distribution of trace elements and chlorophyll *a* in Lake Ontario. *In* Proc. 13th Conf. on Great Lakes Research. Part 2. April 1-3, Buffalo, New York. pp. 659-672.

Environment Canada. 1976. National Inventory of Sources and Emissions of Manganese, Fluoride and Vanadium. Summary of Emissions for 1972. Economic and Technical Review EPS-3-AP-76-1, Air Pollution Control Directorate, Environmental Protection Service, Ottawa. 18 pp. (No longer available.)

Hopkins, L.L., H.L. Cannon, A.T. Musch, R.M. Welch and F.H. Nielson. 1977. Vanadium. Geochem. Environ. 2: 93-107. (Cited in van Zinderen Bakker and Jaworski 1980.)

Kemp, A.L.W., R.L. Thomas, C.I. Dell and J.M. Jacquet. 1976. Cultural impact on the geochemistry of sediments in Lake Erie. J. Fish. Res. Board Can. 33: 440-462.

Lee, K. 1983. Vanadium in the aquatic ecosystem. *In* Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, New York. pp. 155-187.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1974. Vanadium. Medical and Biologic Effects of Environmental Pollutants. Committee on Biologic Effects of Atmospheric Pollutants, National Academy of Sciences, U.S. National Research Council, Washington, D.C. (Cited in van Zinderen Bakker and Jaworski 1980.)

Rose, E.R. 1973. Geology of Vanadium and Vanadiferous Occurrences of Canada. Economic Geology Report No. 17, Energy, Mines and Resources Canada, Ottawa. 130 pp. (Cited in van Zinderen Bakker and Jaworski 1980.)

Schroeder, H.A. 1970. Vanadium. American Petroleum Institute. Air Quality Monograph No. 70-13. 32 pp. (Cited in van Zinderen Bakker and Jaworski 1980.)

Schroeder, H.A. 1974. The Poisons Around Us: Toxic Metals in Food, Air and Water. Indiana University Press, Bloomington, Indiana. (Cited in van Zinderen Bakker and Jaworski 1980.)

Shamberger, R.J. 1978. Beneficial effects of trace elements. *In* Toxicity of Heavy Metals in the Environment. Part 2. Chap. 29. F.W. Oehme (ed.). Marcel Dekker Inc., New York. pp. 689-796. (Cited in van Zinderen Bakker and Jaworski 1980.)

Shaw, D. 1984. Vanadium. *In* Canadian Minerals Yearbook 1982. Mineral Resources Branch, Energy, Mines and Resources Canada, Ottawa. Mineral Report 32.

Strosher, M.T. and E. Peake. 1976. The Evaluation of Waste-waters from an Oil Sands Extraction Plant. AOSERP (Alberta Oil Sands Environmental Research Project) Report No. 5. Calgary, Alberta. 103 pp. (Cited in van Zinderen Bakker and Jaworski 1980.)

van Zinderen Bakker, E.M. and J.F. Jaworski. 1980. Effects of Vanadium in the Canadian Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada. NRCC No. 18132. 94 pp.

Venugopal, B. and T.D. Luckey. 1978. Metal Toxicity in Mammals. Vol. 2. Plenum Press, New York. pp. 220-226. (Cited in van Zinderen Bakker and Jaworski 1980.)

Zoller, W.H., G.E. Gordon, E.S. Gladney and A.G. Jones. 1973. The sources and distribution of vanadium in the atmosphere. *In* Trace Elements in the Environment. Adv. Chem. Ser. No. 123. pp. 31-47. (Cited in van Zinderen Bakker and Jaworski 1980.)

6.2.45 Zinc

6.2.45.1 Uses and Production

Zinc is used in coatings to protect iron and steel (35% of the global production of zinc), in alloys for die casting (25%) and in brass (20%), rolled sheets and strips for dry batteries, roofing and exterior fittings on buildings and some printing processes (Brown 1978).

Canadian zinc mine production in 1984 was estimated at 1 185 000 t. Refined zinc production was estimated at 685 000 t in Canada in 1984. World production for zinc in 1984 was 5 000 000 t. Canadian consumption of zinc in 1984 was approximately 141 600 t (Gauvin 1985).

6.2.45.2 Sources and Pathways for Entering the Aquatic Environment

The principal ores of zinc are sulphides, such as sphalerite and wurtzite (cubic and hexagonal ZnS, respectively), carbonate, also known as smithsonite or calamine ($ZnCO_3$) and silicate, also known as willemite (Zn_2SiO_4) (Browning 1969). In sulphides, zinc often occurs in combination with other elements, particularly iron, copper and lead.

Zinc can enter the environment through both natural and anthropogenic processes (Table 6-64).

6.2.45.3 Environmental Concentrations

Zinc ranks as the 24th most abundant element found in the earth's crust, with an average concentration of 70 $mg{\cdot}kg^{-1}$. The "extractable" zinc concentration in surface waters in Canada usually has a range of approximately <0.001-0.10 $mg{\cdot}L^{-1}$ (rivers) and <0.001-0.05 $mg{\cdot}L^{-1}$ (lakes) (Taylor and Demayo 1980). Environmental concentration ranges for zinc in Canadian surface waters are presented in Table 6-65. In certain waters, such as in mining areas or acidic waters, concentrations 10-1000 times greater can be found. Zinc concentrations in the top few centimetres of bottom sediments of rivers and lakes are 10-700 $mg{\cdot}kg^{-1}$, with averages of approximately 120 $mg{\cdot}kg^{-1}$ (Taylor and Demayo 1980).

6.2.45.4 Forms and Fate in the Aquatic Environment

In aqueous solutions, zinc has an oxidation state of +2 and exhibits amphoteric properties, dissolving in acids to form hydrated Zn(II) cations and in strong bases to form zincate anions, probably of the form $Zn(OH)_4^{2-}$ (Cotton and Wilkinson 1980). Zinc can also form organozinc compounds and complexes with anionic, cationic, neutral and more complex ligands (Aylett 1973). In natural waters, zinc can be found in several forms, such as simple hydrated ions and inorganic and organic complexes (Taylor and Demayo 1980; Spear 1981).

There is not sufficient information on chemical speciation to construct a comprehensive model for the transport and transformation of zinc in the aquatic environment. Early models describing the chemical forms of zinc in simplified aqueous systems are inaccurate, and the existence of several important complexes has yet to be experimentally verified (Spear 1981). However, some general trends are apparent. For example, in most natural waters, zinc will exist mainly as the divalent cation. The presence of organic material can have a dominating effect on the form of zinc in waters of high organic content (U.S. EPA 1979).

In natural waters, zinc occurs in both suspended and dissolved forms. It exists as a simple hydrated ion, inorganic compounds (e.g. $ZnCO_3$), stable organic complexes (e.g. Zn-cysteinate) and adsorbed onto or occluded in inorganic (Zn^{2+}-clay) or organic (Zn^{2+}-humic acids) colloids. The fraction of zinc in each of these forms depends on the pH, the total amount of zinc in water and the presence of other metal ions, organic and inorganic compounds (Florence and Batley 1977).

Table 6-64. Estimated Annual Zinc Input to the Environment from Natural and Anthropogenic Sources

Source	Amount (10^3 t)
Natural	
Weathering	725
Erosion	25
Other	18.5
Total	768.5
Anthropogenic	
Primary zinc production	99
Wood combustion	75
Waste incineration	37
Iron and steel production	35
Other atmospheric emissions	68
Municipal wastewater	100
Total	414

Source: Taylor and Demayo 1980.

Table 6-65. Environmental Concentration Ranges for Zinc in Canadian Surface Waters

Region	Concentration range[1] ($\mu g{\cdot}L^{-1}$)	Number of samples	Sampling year(s)
Pacific	1-130	154	1980-1985
Western	1-290	1588	1980-1985
Central	1-1170	1312	1980-1985
Atlantic	0.1-190	303	1980-1985

[1] Detection limit is 1 $\mu g{\cdot}L^{-1}$ (total).

Source: NAQUADAT 1985.

According to theoretical calculations, the greatest dissolved zinc concentrations in fresh waters are possible at low pH, low alkalinity and high ionic strength (Hem 1972). Chemical speciation in fresh water is influenced primarily by pH and alkalinity (Taylor and Demayo 1980).

Model calculations using measured dissolved concentrations ($\mu mol{\cdot}L^{-1}$) in water samples from Lake Celyn (North Wales) (pH 6.2), (humic ligand, 1.2; Zn, 0.18; Mg, 10; Ca, 26; Mn, 0.35; Ni, 0.02; Co, 0.017; Cu, 0.01; Cd, 0.0036; and Hg, 0.00035 $\mu mol{\cdot}L^{-1}$) showed that 88.8% of the zinc was in the form of free ion (Zn^{2+}), 7% was complexed by the humic ligand and 3.1% was present as bicarbonate, 0.6% as carbonate and 0.5% as sulphate (Mantoura *et al.* 1978).

Model calculations for fresh waters in which both humic substances and inorganic ligands were considered showed that below pH 7, Zn^{2+} was the dominant species, followed by $ZnHCO_3$, $ZnCO_3$, humic complexes and $ZnOH^+$. With increasing pH, the concentrations of $ZnCO_3$, Zn-humic substances and $ZnOH^+$ also increased; however, the concentration of Zn^{2+} and $ZnHCO_3$ decreased. A decrease in alkalinity favoured the free metal ion, whereas increased pH and increased concentrations of humic substances favoured the formation of humic complexes. For example, at a concentration of humic substances of 20 $mg{\cdot}L^{-1}$ and pH 6.5, 8.3% of the zinc was found in humic complexes; however, at pH 8.09 this percentage rose to 64.7. The dissolved zinc concentration, which was also calculated by the model from the solubility of zinc silicate (willemite-Zn_2SiO_4), decreased from approximately 20 $mg \cdot L^{-1}$ at pH 6.5 to about 0.06 $mg \cdot L^{-1}$ at pH 8.09 (Wilson 1978).

Sorption of zinc by hydrous metal oxides, clay minerals and organic materials appears to be an important process in the aquatic environment (U.S. EPA 1979). In the presence of dissolved solids, much of the zinc will be transported in solution as hydrated cations or complex species (Perhac 1974a, b). However, in the presence of suspended solids, much of the zinc will be sorbed to suspended and colloidal particles (Kubota *et al.* 1974; Steele and Wagner 1975). Coprecipitation and sorption of dissolved zinc by hydrous iron and manganese oxides can occur if high concentrations of reduced iron and manganese are introduced into aerobic surface waters (Lee 1975). Above pH 7.0, metal oxides, clay and apatite are efficient adsorbers, capable of binding 90-100% of the zinc (Spear 1981). In general, zinc adsorption is not anticipated below pH 6.0 (Jenne 1968), although some clays, particularly montmorillonite, can adsorb zinc at a lower pH (Farrah and Pickering 1977). In anaerobic systems, hydrous metal oxides can solubilize and release zinc ions (Sims and Patrick 1978). Adsorptive capacity is also expected to decrease with increasing ionic strength (James and MacNaughton 1977). Under anaerobic conditions and in the presence of sulphur, insoluble zinc sulphide is produced. However, if redox potential is increased, sulphide oxidation will result in zinc dissolution and remobilization (Jonasson and Timperley 1975).

There is no evidence to suggest that either photolysis or volatilization plays a significant role in the removal of zinc from the water column (U.S. EPA 1979).

Zinc is distributed throughout the biotic component of the aquatic environment. As zinc is an essential element, it is readily bioaccumulated (U.S. EPA 1980). Although most of the available information pertains to marine environments, it is expected that residues in freshwater organisms will not be significantly different from those found in marine organisms (U.S. National Research Council 1979). Bioconcentration factors in the order of 10^3 for freshwater plants and fish (Chapman *et al.* 1968) and 10^4 for freshwater invertebrates (Chapman *et al.* 1968; Namminga and Wilham 1977) have been reported. Bioconcentration factors for mayfly (*Ephemerella grandis*) (Nehring 1976), stonefly (*Pteronarcys californica*) (Nehring 1976), Atlantic salmon (*Salmo salar*) (Farmer *et al.* 1979) and flagfish (*Jordanella floridae*) (Gauvin 1985) were 1130, 107, 51 and 432, respectively.

Zinc is important in biological systems, being involved in nucleic acid synthesis and occurring in many enzymes. Biomethylation of zinc in aquatic systems probably does not occur. The presence of biogenically derived ligands, however, will affect the transport of zinc in some aquatic ecosystems (U.S. EPA 1979).

6.2.45.5 References

Aylett, B.J. 1973. Group IIB. *In* Comprehensive Inorganic Chemistry. Vol. 3. J.C. Bailar, Jr., H.J. Emeléus, Sir Ronald Nyholm and A.F. Trotman-Dickenson (eds.). Pergamon Press, Oxford. pp. 187-328.

Brown, D.H. 1978. Zinc. Can. Min. J. 99(2): 70-77.

Browning, E. 1969. Zinc. *In* Toxicity of Industrial Metals. 2nd edition. Butterworths, London. pp. 348-355.

Chapman, W.H., H.L. Fisher and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, California. UCRL-50564. 46 pp. (Cited in U.S. EPA 1979.)

Cotton, F.A. and A. Wilkinson. 1980. Advanced Inorganic Chemistry. 4th edition. John Wiley & Sons, New York. 1396 pp.

Farmer, G.J., D. Ashfield and H.S. Samant. 1979. Effects of zinc on juvenile Atlantic salmon *Salmo salar*: Acute toxicity, food intake, growth and bioaccumulation. Environ. Pollut. 19: 103-117.

Farrah, H. and W.F. Pickering. 1977. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water Air Soil Pollut. 8: 189-197.

Florence, T.M. and G.E. Batley. 1977. Determination of the chemical forms of trace metals in natural waters, with special reference to copper, lead, cadmium and zinc. Talanta 24: 151-158.

Gauvin, M.J. 1985. Zinc. Can. Min. J. 106(2): 52, 54.

Hem, J.D. 1972. Chemistry and occurrence of cadmium and zinc in surface waters and ground water. Water Resour. Res. 8: 661-678.

James, R.O. and M.G. MacNaughton. 1977. The adsorption of aqueous heavy metals on inorganic minerals. Geochim. Cosmochim. Acta 41: 1549-1555.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. Adv. Chem. Ser. 73: 337-387.

Jonasson, I.R. and M.H. Timperley. 1975. Field observations on the transport of heavy metals in sediments: discussion. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Toronto, Ontario. pp. 97-102.

Kubota, J., E.L. Mills and R.T. Oglesby. 1974. Lead, Cd, Zn, Cu and Co in streams and lake waters of Cayuga Lake Basin, New York. Environ. Sci. Technol. 8: 243-248.

Lee, G.F. 1975. Role of hydrous metal oxides in the transport of heavy metals in the environment. *In* Heavy Metals in the Aquatic Environment. P.A. Krenkel (ed.). Pergamon Press, Toronto, Ontario. pp. 137-147.

Mantoura, R.F.C., A. Dickson and J.P. Riley. 1978. The complexation of metals with humic materials in natural waters. Estuarine Coastal Mar. Sci. 6: 387-408.

Namminga, H. and J. Wilham. 1977. Heavy metals in water, sediments and chironomids. J. Water Pollut. Control Fed. 49: 1725-1731.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Nehring, B.R. 1976. Aquatic insects as biological monitors of heavy metal pollution. Bull. Environ. Contam. Toxicol. 15: 147-154.

Perhac, R.M. 1974a. Water transport of heavy metals in solution and by different sizes of particulate solids. Proj. No. 023, Univ. Tenn. Water Resour. Res. Cent., Knoxville, Tennessee. (Cited in U.S. EPA 1979.)

Perhac, R.M. 1974b. Heavy Metal Distribution in Bottom Sediments and Water in the Tennessee River-Loudon Lake Reservoir System. Proj. No. 40, Univ. Tenn. Water Resour. Cent., Knoxville, Tennessee. (Cited in U.S. EPA 1979.)

Sims, J.L. and W.H. Patrick, Jr. 1978. The distribution of micronutrient cations in soil under conditions of varying redox potential and pH. Soil Sci. Soc. Am. J. 42: 258-262.

Spear, P.A. 1981. Zinc in the Aquatic Environment: Chemistry, Distribution and Toxicology. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 17589. 145 pp.

Steele, K.F. and A.H. Wagner. 1975. Trace metal relationships in bottom sediments of a freshwater stream – the Buffalo River, Arkansas. J. Sediment. Petrol. 45: 310-319. (Cited in U.S. EPA 1979.)

Taylor, M.C. and A. Demayo. 1980. Zinc. *In* Guidelines for Surface Water Quality. Vol. 1. Inorganic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

U.S. EPA. 1979. Zinc. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 19-1 to 19-21.

U.S. EPA. 1980. Ambient Water Quality Criteria for Zinc. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-079.

U.S. National Research Council. 1979. Zinc. National Academy of Sciences. University Park Press, Baltimore, Maryland. 471 pp.

Wilson, D.E. 1978. An equilibrium model describing the influence of humic materials on the speciation of Cu^{2+}, Zn^{2+} and Mn^{2+} in freshwaters. Limnol. Oceanogr. 23: 499-507.

6.3 ORGANIC PARAMETERS

6.3.1 Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) of water may be defined as the amount of oxygen required for aerobic microorganisms to oxidize organic matter to a stable inorganic form. The determination of BOD is an empirical test in which standardized laboratory procedures are used to quantify the relative oxygen requirement of a water sample. The BOD test measures the oxygen required for the microbial oxidation of organic matter (carbonaceous demand) and the oxygen required for the oxidation of inorganic material, such as sulphides and ferrous iron. It may also measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand). BOD is usually reported as the amount of oxygen consumed over a specified period of time at a specified incubation temperature. Five days has been accepted as the standard incubation time, with 20°C the standard temperature; hence, oxygen demand is usually reported as BOD_5 (McNeely *et al.* 1979; Greenberg *et al.* 1981).

Because BOD measures only the amount of oxygen consumed in a standardized test, it does not indicate the presence of nonbiodegradable matter, nor does it account for the toxic or inhibitory effect of materials on microbial activity (McNeely *et al.* 1979; Greenberg *et al.* 1981).

Environmental concentration ranges for BOD in Canadian surface waters are presented in Table 6-66.

Table 6-66. Environmental Concentration Ranges for BOD in Canadian Surface Waters

Region	Concentration range[1] (mg·L⁻¹)	Number of samples	Sampling year(s)
Pacific	0-470	681	Prior to 1980
Western	0-104	3231	Prior to 1980
Central	0-450	1743	Prior to 1980
Atlantic	0.3-9	22	1980

[1] Detection limit is 0.01 mg·L⁻¹.

Source: NAQUADAT 1985.

6.3.1.1 References

Greenberg, A.E., J.J. Connors and D. Jenkins (eds.). 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Oxygen – biochemical oxygen demand. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 32.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

6.3.2 Chemical Oxygen Demand

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter content of a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate. Using the dichromate reflux method, most organic compounds are oxidized to 95-100% of their theoretical value. However, some organic compounds are not oxidized, including pyrimidine and organic compounds that lack sufficient contact time because of their volatility. Whereas the carbonaceous portion of nitrogen-containing material is oxidized, ammonia is not oxidized unless in the presence of significant concentrations of chloride. Being a nonspecific test, a COD determination does not indicate the nature of the oxidizable material, nor does it differentiate between organic and inorganic material present in a water sample (McNeely *et al.* 1979; Greenberg *et al.* 1981).

Environmental concentration ranges for COD in Canadian surface waters are presented in Table 6-67.

6.3.2.1 References

Greenberg, A.E., J.J. Connors and D. Jenkins (eds.). 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Oxygen – chemical oxygen demand. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 32-33.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

6.3.3 Diphenylhydrazine

6.3.3.1 Uses and Production

The hydrochloride of 1,2-diphenylhydrazine is used as a reagent in the manufacture of the sugars arabinose and lactose. It is also used in the synthesis of phenylbutazone and as a starting material in the manufacture of benzidine, an intermediate in the production of dyes (U.S. EPA 1980; Verschueren 1983). Azobenzene has been used as an acaricide (Worthing 1983), but it is not registered for use as such in Canada (Agriculture Canada 1984).

No information is available on production or importation of diphenylhydrazine in Canada.

6.3.3.2 Sources and Pathways for Entering the Aquatic Environment

Although limited quantitative information is available, it is known that diphenylhydrazine/azobenzene may enter the aquatic environment during manufacture, use and disposal.

1,2-Diphenylhydrazine was detected in 5 of 17 samples taken from the St. Clair River in 1979 and 1980. The concentrations, however, were not measured. Total diphenylhydrazine loadings from 14 industrial and municipal outfalls to the St. Lawrence River at Cornwall, Ontario, were estimated at more than 0.02 kg·d⁻¹ (Environment Canada 1984).

Table 6-67. **Environmental Concentration Ranges for COD in Canadian Surface Waters**

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	10-105	311	Prior to 1980
Western	0.03-197	560	Prior to 1980
Central	10-70	323	Prior to 1980
Atlantic	16-59	19	1980

[1] Detection limit is 1 mg·L^{-1}.

Source: NAQUADAT 1985.

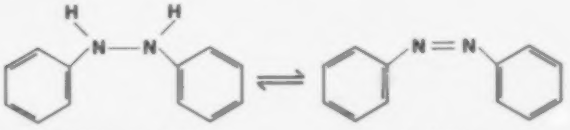
6.3.3.3 Environmental Concentrations

1,2-Diphenylhydrazine was detected in drinking water (1 µg·L^{-1}) in the United States, and azobenzene was detected in industrial effluents (Shackelford and Keith 1976).

2,6-Diphenylhydrazine was not detected in three samples of St. Clair River surface water taken in 1979 (Munro *et al.* 1985). Similarly, no detectable concentrations of 1,2-diphenylhydrazine were found in the St. Lawrence River at Cornwall, Ontario, in 1980 (Environment Canada 1984).

6.3.3.4 Forms and Fate in the Aquatic Environment

In aerated, aqueous solutions, 1,2-diphenylhydrazine occurs in reversible redox equilibrium with azobenzene (Figure 6-3) (Griffiths 1972; Rao and Hayon 1976). Because azobenzene predominates in well-aerated waters (Blackadder and Hinshelwood 1957; Rao and Hayon 1976), an examination of the environmental fate of 1,2-diphenylhydrazine must include both chemical forms (Griffiths 1972; Rao and Hayon 1976). Some physical-chemical properties of 1,2-diphenylhydrazine and azobenzene appear in Table 6-68.



1,2-Diphenylhydrazine

Azobenzene

Figure 6-3. **Equilibrium between 1,2-diphenylhydrazine and azobenzene.**

1,2-Diphenylhydrazine and azobenzene have relatively high octanol/water partition coefficients (Fujita *et al.* 1964; Leo *et al.* 1971) depending upon redox potential and should be relatively strongly sorbed by organic particulates (U.S. EPA 1979). Azobenzene has been found to be strongly sorbed to silicate minerals (Sato 1956; Zubareva *et al.* 1974).

Because azobenzene has a very low vapour pressure (U.S. EPA 1979; Verschueren 1983) and a high affinity for lipophilic material (Leo *et al.* 1971), volatilization from the water column is not expected to be significant. Likewise, 1,2-diphenylhydrazine should be relatively nonvolatile (U.S. EPA 1979).

The biodegradation of 1,2-diphenylhydrazine and azobenzene in the aquatic environment has not been studied (U.S. EPA 1979). Although their calculated octanol/water partition coefficients indicate the possibility for bioaccumulation, residues in aquatic organisms have not been examined (U.S. EPA 1980).

6.3.3.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Blackadder, D.A. and C. Hinshelwood. 1957. The kinetics of the rearrangement and oxidation of hydrazobenzene in solution. J. Chem. Soc. 1957: 2898-2903. (Cited in U.S. EPA 1979.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Fujita, T., J. Iwasa and C. Hansch. 1964. A new substituent constant, π, derived from partition coefficients. J. Am. Chem. Soc. 86: 5175-5180. (Cited in U.S. EPA 1979.)

Griffiths, J. 1972. Photochemistry of azobenzene and its derivatives. Chem. Soc. Rev. 1: 481-493.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-612.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

Rao, P.S. and E. Hayon. 1976. Correlation between ionization constants of organic free radicals and electrochemical properties of parent compounds. Anal. Chem. 48: 564-568.

Sato, C. 1956. Adsorption of some azo dyes by montmorillonite in relation to the composite character of its surface. J. Chem. Soc. Jpn., Pure Chem. Sect. 77: 716-720. (Cited in U.S. EPA 1979.)

Shackelford, W.M. and L.H. Keith. 1976. Frequency of Organic Compounds Identified in Water. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/4-76-062.

U.S. EPA. 1979. 1,2-Diphenylhydrazine (Hydrazobenzene). *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 104-1 to 104-9.

U.S. EPA. 1980. Ambient Water Quality Criteria for Diphenylhydrazine. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-062.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 570.

Zubareva, N.A., A.V. Kiselev and V.L. Lygin. 1974. Ultraviolet spectra of organic bases adsorbed on the surfaces of pure and alumina-modified silicas. Kinet. Katal. 15: 483-487. (Cited in U.S. EPA 1979.)

6.3.4 Halogenated Aliphatic Compounds

6.3.4.1 Chlorinated Ethanes

6.3.4.1.1 Uses and Production

Chlorinated ethanes are used as industrial solvents and in the production of other organochlorine compounds. They are

Table 6-68. Physical-chemical Properties of 1,2-Diphenylhydrazine and Azobenzene

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility ($mg \cdot L^{-1}$ (°C))	Octanol/water partition coefficient (log P_{ow})
1,2-Diphenylhydrazine	184.23	126	—	—	—	3.03
Azobenzene	182.23	68.3	293	1.3×10^{-1} (103)	0.252 (20)	3.82

Sources: U.S. EPA 1979; Verschueren 1983.

also used as dry-cleaning agents, as anesthetics, in the manufacturing of plastics and textiles and in the production of tetraethyllead and vinyl chloride. More than 80% of the 1,2-dichloroethanes produced in the United States is used to manufacture vinyl chloride and other chlorinated chemicals. Low cost and excellent properties as solvents, degreasing agents, fumigants and cutting fluids make chloroethanes a common constituent in many products used by the general public (U.S. EPA 1975a).

Production and importation data in Canada for chloroethanes are presented in Table 6-69. In 1983, 15 100 t of chloroethane were consumed in Canada, and 2500 t were exported (CORPUS Information Services 1984).

6.3.4.1.2 Sources and Pathways for Entering the Aquatic Environment

Chloroethanes are formed in small amounts by the aqueous chlorination of effluents. The main sources to the environment, however, are industrial emissions and the discharge of liquid industrial wastes (U.S. EPA 1980). Ontario discharges 300 t of dichloroethane to the Great Lakes annually. Atmospheric emissions of this compound are of similar magnitude (CORPUS Information Services 1984). The U.S. gross annual discharge and loss to the environment of various chloroethanes range from about 75 to 2500 t (U.S. EPA 1976c). Nonpoint sources of chloroethanes involve the use of such products as paint and varnish removers (U.S. EPA 1980).

6.3.4.1.3 Environmental Concentrations

Several chloroethanes, including 1,2-dichloroethane and 1,1,1-trichloroethane, have been detected in both raw and finished waters in the United States. In finished water, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane and 1,1,1,2-tetrachloroethane were identified. In the U.S.A., average concentrations of chloroethanes in chlorinated tap water range from 0.1 to 8.5 $\mu g \cdot L^{-1}$ (U.S. EPA 1975b). 1,1-Dichloroethane was found in one sample of Cornwall drinking water at a concentration of 6.5 $\mu g \cdot L^{-1}$ (Environment Canada 1984). Several volatile halocarbon compounds were identified in the Niagara River and in Lake Ontario during sampling in 1981. 1,1,1-Trichloroethane was found in Niagara River water samples at a mean concentration of 7 ± 4 $ng \cdot L^{-1}$. In Lake Ontario water, its concentration varied from <2 to 180 $ng \cdot L^{-1}$ (Kaiser *et al.* 1983). Concentrations of various chloroethanes found in surface waters in Canada are presented in Table 6-70.

Table 6-69. Production and Importation of Various Chloroethanes in Canada

Compound	Year	Production (t)	Importation (t)
Chloroethane (ethyl chloride)	1981	20 000	936
	1982	22 000	100
	1983	17 500	10
1,2-Dichloroethane (ethylene dichloride)	1981	NA[1]	138
	1982	NA	63
	1983	670 000	20
1,1,1-Trichloroethane	1981	NA	2415
	1982	NA	1758
	1983	12 500	3200
1,1,2-Trichloroethane	1981	NA	97
	1982	NA	81

[1] NA = not available.

Sources: Statistics Canada 1983; CORPUS Information Services 1984.

Table 6-70. Environmental Concentration Ranges for Various Chloroethanes in Canadian Surface Waters

Compound	Location	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples
1,1-Dichloroethane	St. Clair River	Trace[1]-2	2
	Cornwall	Trace[2]-17.3	5
1,2-Dichloroethane	St. Clair River	Trace-13.0	13
	Cornwall	Trace	2
Dichloroethanes (unspecified isomers)	Cornwall	Trace-5.5	3
1,1,1-Trichloroethane	St. Clair River	Trace-0.02	2
	Cornwall	Trace	5
		323.5 (maximum upper limit)	1
1,1,2-Trichloroethane	Cornwall	Trace	2
Tetrachloroethane	St. Clair River	Trace-41	2
	Great Lakes	1-44	—

[1] 0.05-0.1 $\mu g \cdot L^{-1}$ for St. Clair River near Sarnia, Ontario.
[2] <1 $\mu g \cdot L^{-1}$ for St. Lawrence River at Cornwall, Ontario.

Sources: IJC 1981; Bonner and Meresz 1981; Environment Canada 1984.

Table 6-71. Physical-chemical Properties of Some Chlorinated Ethanes

Compound	Alternate names	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa) at 20°C	Water solubility ($mg \cdot L^{-1}$) at 20°C	Octanol/water partition coefficient (log P_{ow})
Chloroethane	Ethyl chloride	C_2H_5Cl	64.52	−136.4	12.27	133	5740	1.54[1]
1,1-Dichloroethane	Ethylidine chloride	$C_2H_4Cl_2$	98.96	−96.98	57.28	24	5500	1.79[2]
1,2-Dichloroethane	Ethylene dichloride	$C_2H_4Cl_2$	98.96	−35.36	83.47	8.1	8690	1.48[3]
1,1,1-Trichloroethane	Methyl chloroform	$C_2H_3Cl_3$	133.41	−30.41	74.1	12.8	480[4]	2.17[5]
1,1,2-Trichloroethane	Vinyl trichloride	$C_2H_3Cl_3$	133.41	−36.5	133.77	2.5	4500	2.17[5]
1,1,2,2-Tetrachloroethane	Acetylene tetrachloride	$C_2H_2Cl_4$	167.85	−36	146.2	0.7	2900	2.56[5]
1,1,1,2-Tetrachloroethane	Tetrachloroethane	$C_2H_2Cl_4$	167.85		138			
Pentachloroethane	Pentalin	C_2HCl_5	202.3	−29	162	0.5		
Hexachloroethane	Perchloroethane	C_2Cl_6	236.74	sublimes	186	0.1	50	3.34[5]

[1] Leo *et al.* 1971.

[2] Hansch *et al.* 1975.

[3] Radding *et al.* 1977.

[4] Pearson and McConnell 1975.

[5] Tute 1971.

Sources: U.S. EPA 1979; Verschueren 1983.

6.3.4.1.4 Forms and Fate in the Aquatic Environment

Chlorinated ethanes (chloroethanes) are low-molecular-weight saturated compounds containing two carbon atoms, in which one or more hydrogen atoms have been substituted with chlorine; mono-, di-, tri-, tetra-, penta- and hexachloroethanes are possible. Some physical and chemical properties of chloroethanes appear in Table 6-71. With the exception of hexachloroethane, all chloroethanes are low-boiling liquids. Most chloroethanes are relatively volatile and water-soluble. In general, both volatility and water solubility decrease with increasing chlorine substitution. Although little reliable information is available on the fate of these compounds in the aquatic environment, volatilization (followed by atmospheric oxidation) is considered to be the primary removal process (U.S. EPA 1979).

Little information is available on sorption of chloroethanes to surfaces. Because the lower chlorinated compounds have slight affinities for lipophilic materials (Leo *et al.* 1971; Tute 1971; Pearson and McConnell 1975), sorption to organic-rich material is considered to be minimal. In laboratory tests, little or no sorption to inorganic or organic material was observed (Dilling *et al.* 1975). No selective concentration of chloroethanes was observed in sediments during field surveys (Pearson and McConnell 1975; McConnell *et al.* 1975). Whereas coarse gravel had little adsorptive capacity for 1,1,1-trichloroethane, sediments rich in organic detritus had a much higher adsorptive capacity (McConnell *et al.* 1975).

Direct photolysis, oxidation and hydrolysis are not expected to be significant removal processes for chloroethanes in the aquatic environment (Dilling *et al.* 1975; Radding *et al.* 1977; U.S. EPA 1979).

Because chloroethanes have high vapour pressures, volatilization is considered to be the primary removal process of these compounds from the water column. Evaporative half-lives of 0.5-1 h have been measured for several chloroethanes at aqueous concentrations of approximately 1 $mg \cdot L^{-1}$ (Dilling *et al.* 1975; Dilling 1977). Once in the troposphere, mono-, di- and trichloroethanes may be oxidized with half-lives of 1 to several months (Lillian *et al.* 1975; Howard and Evenson 1976; McConnell and Schiff 1978; Hanst 1978). No information for tetra-, penta- and hexachloroethane is available; however, it is expected that their atmospheric oxidation would be slower than that of the lower chlorinated ethanes (U.S. EPA 1979).

Little information on biodegradation is available. Little or no degradation of chloroethanes was found during standard BOD (biochemical oxygen demand) bottle tests (Pearson and McConnell 1975; McConnell *et al.* 1975). With the exception of hexachloroethane, most chloroethanes have low octanol/water partition coefficients, indicating only a slight tendency to bioaccumulate. Steady-state bioconcentration factors for several chloroethanes were measured for bluegill sunfish (*Lepomis macrochirus*) during exposures for 14-28 d: 1,2-dichloroethane, 2; 1,1,1-trichloroethane, 9; 1,1,2,2-tetrachloroethane, 8; pentachloroethane, 67; and hexachloroethane, 139. All the chloroethanes tested had a biological half-life below 2 d, indicating rapid depuration (U.S. EPA 1978, 1980).

6.3.4.1.5 References

Bonner, R.F. and O. Meresz. 1981. Identification and Quantification of Organic Compounds. Organic Trace Contaminants Section, Ontario Ministry of the Environment, Toronto, Ontario.

CORPUS Information Services. 1984. Ethyl chloride. Ethylene dichloride. CPI Product Profiles. Don Mills, Ontario.

Dilling, W.L. 1977. Interphase transfer processes II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11: 405-409.

Dilling, W.L., N.B. Tefertiller and G.J. Kallos. 1975. Evaporation rates of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9: 833-838.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Hansch, C., A. Vittoria, C. Silipo and P.Y.C. Jow. 1975. Partition coefficients and the structure-activity relationship of the anesthetic gases. J. Med. Chem. 18: 546-548.

Hanst, P.L. 1978. Halogenated pollutants. Part II. Noxious trace gases in the air. Chemistry 51: 6-12.

Howard, C.J. and K.M. Evenson. 1976. Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296°K. J. Chem. Phys. 64: 4303-4306.

IJC. 1981. Annual Report. Report to the Great Lakes Water Quality Board/Great Lakes Science Advisory Board. International Joint Commission, Windsor, Ontario.

Kaiser, K.L.E., M.E. Comba and H. Huneault. 1983. Volatile halocarbon contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Res. 9: 212-223.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

Lillian, D., H.B. Singh, A. Appleby, L. Lobban, R. Arnts, R. Gumpert, R. Hague, J. Toomey, J. Kazazis, M. Antell, D. Hansen and B. Scott. 1975. Atmospheric fates of halogenated compounds. Environ. Sci. Technol. 9: 1042-1048.

McConnell, G., D.M. Ferguson and C.R. Pearson. 1975. Chlorinated hydrocarbons and the environment. Endeavor 34: 13-18.

McConnell, J.C. and H.I. Schiff. 1978. Methyl chloroform: Impact on stratospheric ozone. Science 199: 174-177.

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B 189: 305-322.

Radding, S.B., D.H. Lice, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003. 147 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6: 1-77.

U.S. EPA. 1975a. Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Hydrocarbons. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA 450/3-75-073, NTIS-247115.

U.S. EPA. 1975b. Analysis of carbon and resin extracts. *In* New Orleans Area Water Supply Study. U.S. Environmental Protection Agency, Dallas, Texas. EPA/906/9-75/003.

U.S. EPA. 1975c. Identification of Organic Compounds in Effluents from Industrial Sources. U.S. Environmental Protection Agency. EPA 560/3-75-002.

U.S. EPA. 1978. In-depth Studies in Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency. Contract No. 68-01-4646.

U.S. EPA. 1979. Chloroethane. 1,1-Dichloroethane. 1,2-Dichloroethane. 1,1,1-Trichloroethane. 1,1,2-Trichloroethane. 1,1,2,2-Tetrachloroethane. Hexachloroethane. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 42-1 to 42-9, 43-1 to 43-10, 44-1 to 44-10, 45-1 to 45-12, 46-1 to 46-9, 47-1 to 47-9, and 48-1 to 48-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Chlorinated Ethanes. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-029.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Table 6-72. Production and Importation of Various Chloroethylenes in Canada

Compound	Year	Production (t)	Importation (t)
Trichloroethylene	1981	NA[1]	1253
	1982	NA	1877
	1983	13 000	3200
Tetrachloroethylene (Perchloroethylene)	1981	NA	717
	1982	NA	2272
	1983	23 000	3700

[1] NA = not available.

Sources: Statistics Canada 1983; CORPUS Information Services 1984.

6.3.4.2 Chlorinated Ethylenes

6.3.4.2.1 Uses and Production

Chlorinated ethylenes (chloroethylenes) are produced in large quantities and are widely used in industry (U.S. EPA 1980a, b, c). 1,1-Dichloroethylene is used as a chemical intermediate in the synthesis of methylchloroform. The production of polyvinylidene chloride copolymers for barrier coatings (e.g. Saran Wrap) for the food packaging industry also uses 1,1-dichloroethylene. The impermeability and heat-seal characteristics of Saran coatings make them useful in the manufacture of nonflammable synthetic fibres. The coating of steel pipes and structures and the interior coating of ship tanks, railroad cars and fuel storage tanks are other uses of 1,1-dichloroethylene (U.S. EPA 1980b).

Dichloro- and trichloroethylenes have anesthetic properties and may be used during short-term surgical procedures (U.S. EPA 1980a, b). Trichloroethylene is used mainly as a degreasing agent, as well as in household and industrial dry-cleaning solvents and as extractive solvents for food. The relative chemical stability, nonflammability, volatility and low water solubility of this compound make it a very useful solvent, and it is widely used, with an annual U.S. production of 234 000 t (U.S. EPA 1980a, b). Tetrachloroethylene is primarily used as a solvent in dry-cleaning, and to a lesser extent as a degreasing solvent in metal industries (U.S. EPA 1980c).

Production and importation data in Canada for various chloroethylenes are presented in Table 6-72.

6.3.4.2.2 Sources and Pathways for Entering the Aquatic Environment

The major route by which chlorinated ethylenes enter the environment is volatilization during production and use. Their presence in water may result from direct discharge or from atmospheric deposition. These compounds may also be formed during the chlorination of water (McConnell *et al.* 1975; U.S. EPA 1979).

1,1-Dichloroethylene may migrate into water from discarded vinylidene chloride polymer materials or through the decomposition of 1,1,1-trichloroethylene (U.S. EPA 1980b). Trichloroethylene, as a solvent for food extractions, may be found

Table 6-73. Environmental Concentration Ranges for Various Chloroethylenes in Canadian Surface Waters

Compound	Location	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples
1,1-Dichloroethylene	Cornwall	Trace[1]	2
Trichloroethylene	St. Clair River	Trace[2] – 1	10
	Cornwall	Trace	4
	Great Lakes	Trace – 10	—
Tetrachloroethylene	St. Clair River	Trace – 2	29
	Cornwall	Trace	3

[1] <1 $\mu g \cdot L^{-1}$ for St. Lawrence River at Cornwall, Ontario.
[2] 0.05-0.1 $\mu g \cdot L^{-1}$ for St. Clair River near Sarnia, Ontario.

Sources: IJC 1981; Bonner and Meresz 1981; Environment Canada 1984.

in foodstuffs such as decaffeinated coffee and other beverages, as well as some meat, fruit and vegetables (U.S. EPA 1980a). Production plants, consumer industries and sewage are sources of tetrachloroethylene via aqueous effluents (U.S. EPA 1980c). Ontario discharges approximately 13.6 t of trichloroethylene and 25 t of tetrachloroethylene into the Great Lakes annually (IJC 1981).

6.3.4.2.3 Environmental Concentrations

Chloroethylenes have been detected in both raw and finished drinking waters in the United States. *Cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene at concentrations of 16 and 1 $\mu g \cdot L^{-1}$, respectively, were detected in Miami drinking water (U.S. EPA 1980b). Trichloroethylene has been detected in the atmosphere, in food, in human tissues and in the aquatic environment (U.S. EPA 1980a).

The highest levels of tetrachloroethylene are found in occupational environments involving dry-cleaning and metal degreasing. Drinking water concentrations as high as 3.1 $\mu g \cdot L^{-1}$ (U.S. EPA 1980c) have been detected in the U.S.A., and contaminated groundwater in Switzerland contained concentrations of 954 $\mu g \cdot L^{-1}$ (Giger and Molnar-Kubica 1978). Concentrations of various chloroethylenes found in surface waters in Canada are presented in Table 6-73. Trichloroethylene was found in water samples collected from the central and eastern basins of Lake Erie in 1977 and 1978. Mean concentration (standard deviation) was 11 ± 9 $ng \cdot L^{-1}$ for 1977 and 20 ± 13 $ng \cdot L^{-1}$ for 1978 (Kaiser and Valdmanis 1979). Several halogenated ethylenes were also identified in the Niagara River and in Lake Ontario. Concentrations of 9 ± 65 $ng \cdot L^{-1}$ tetrachloroethylene were found in Lake Ontario in 1981. In addition, trichloroethylene and tetrachloroethylene were found in the Niagara River at concentrations of 5 ± 3 and 36 ± 47 $ng \cdot L^{-1}$, respectively (Kaiser *et al.* 1983).

6.3.4.2.4 Forms and Fate in the Aquatic Environment

Chlorinated ethylenes are unsaturated, low-molecular-weight C_2 compounds in which one or more hydrogen atoms have been replaced with chlorine; mono-, di-, tri- and tetrachloro- compounds are possible. Some physical and chemical properties of chloroethylenes appear in Table 6-74. With the exception of monochloroethylene, all chlorinated ethylenes are low-boiling liquids that have high vapour pressures and are moderately soluble in water. Vapour pressures and water solubilities decrease with increasing chlorine substitution. Although little information is available on the fate of these compounds in the aquatic environment, volatilization (followed by atmospheric oxidation) is considered to be the primary removal mechanism (U.S. EPA 1979).

Monochloroethylene was not sorbed onto particulate matter (U.S. EPA 1974). Limited sorption was found for tri- and tetrachloroethylene (Dilling *et al.* 1975). In field surveys, no selective concentration by sediments of tri- and tetrachloroethylene was found (Pearson and McConnell 1975). Coarse gravel was found to have no sorptive capacity for tri- and tetrachloroethylene, whereas sediments rich in organic detritus did have a high adsorptive capacity (McConnell *et al.* 1975).

Table 6-74. Physical-chemical Properties of Chlorinated Ethylenes

Compound	Alternate names	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa) at 20°C	Water solubility ($mg \cdot L^{-1}$) at 20°C	Octanol/water partition coefficient (log P_{ow})
Chloroethylene	Vinyl chloride	C_2H_3Cl	62.50	−153.8	−13.37	354.6 (25°C)	1.1 (25°C)	0.60[1]
1,1-Dichloroethylene	Vinylidine chloride	$C_2H_2Cl_2$	96.94	−122.1	37	78.8 (25°C)	60[2] (10°C)	1.48[3]
1,2-Dichloroethylene		$C_2H_2Cl_2$	96.94	−50	47.5	26.7 (14°C)	600	1.48[3]
Trichloroethylene	Ethylene trichloride	C_2HCl_3	131.39	−73	87	7.7[2]	1100[2]	2.29[4]
Tetrachloroethylene	Perchloroethylene	C_2Cl_4	165.83	−22.7	121	1.9[2]	150[2] 200[6]	2.88[5]

[1] Radding *et al.* 1977.
[2] Pearson and McConnell 1975.
[3] Tute 1971.
[4] Leo *et al.* 1971.
[5] Neely *et al.* 1974.
[6] Chiou *et al.* 1977.

Sources: U.S. EPA 1979; Verschueren 1983.

Direct photolysis (Jensen and Rosenberg 1975; Hill *et al.* 1976), oxidation (Hill *et al.* 1976), and hydrolysis (U.S. EPA 1974; Dilling *et al.* 1975) are not considered to be important removal processes for chloroethylenes in the aquatic environment. Monochloroethylene may be photolyzed in the presence of a photosensitizing agent (Hill *et al.* 1976); however, the environmental significance of this reaction has not been examined (U.S. EPA 1979).

Volatilization is the principal process for removal of chloroethylenes from the aquatic environment (U.S. EPA 1979). Evaporative half-lives below 1 h for chloroethylenes at aqueous concentrations of approximately 1 $mg{\cdot}L^{-1}$ at 25°C have been reported (Dilling 1977). Once in the troposphere, chloroethylenes are rapidly oxidized with half-lives ranging from 4 d to 8 weeks (Pearson and McConnell 1975; Yung *et al.* 1975; Gay *et al.* 1976; Dilling *et al.* 1976).

Few data are available on the biodegradation of chloroethylenes in the aquatic environment. Monochloroethylene was found to be resistant to degradation by bacteria and fungi (Hill *et al.* 1976). Other chloroethylenes are considered to be persistent with respect to biodegradation (Pearson and McConnell 1975). Because most of the chloroethylenes have small octanol/water partition coefficients, bioaccumulation is expected to be low. A steady-state bioconcentration factor of 17 was found for trichloroethylene upon exposure of bluegills (*Lepomis macrochirus*) for 14 d; likewise, a bioconcentration factor of 49 after a 21-d exposure was found for tetrachloroethylene. Depuration rates were rapid for both compounds, with half-lives of less than 1 d (U.S. EPA 1978, 1980b, c).

6.3.4.2.5 References

Bonner, R.F. and O. Meresz. 1981. Identification and Quantification of Organic Compounds. Organic Trace Contaminants Section, Ontario Ministry of the Environment, Toronto, Ontario.

Chiou, C.T., V.H. Freed, D.W. Schmedding and R.L. Kohnert. 1977. Partition coefficient and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11: 475-478.

CORPUS Information Services. 1984. Trichloroethylene. Tetrachloroethylene. CPI Product Profiles. Don Mills, Ontario.

Dilling, W.L. 1977. Interphase transfer processes II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with technical predictions. Environ. Sci. Technol. 11: 405-409.

Dilling, W.L., N.B. Tefertiller and G.J. Kallos. 1975. Evaporation rates of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9: 833-838.

Dilling, W.L., C.J. Bredeweg and N.B. Tefertiller. 1976. Simulated atmospheric photodecomposition rates of methylene chloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other compounds. Environ. Sci. Technol. 10: 351-356.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Gay, B.W., Jr., P.L. Hanst, J.J. Bufalini and R.C. Noonan. 1976. Atmospheric oxidation of chlorinated ethylenes. Environ. Sci. Technol. 10: 58-67.

Giger, W. and E. Molnar-Kubica. 1978. Tetrachloroethylene in contaminated ground and drinking waters. Bull. Environ. Contam. Toxicol. 19: 475-480.

Hill, J., IV, H.P. Kollig, D.F. Paris, N.L. Wolfe and R.G. Zepp. 1976. Dynamic Behaviour of Vinyl Chloride in Aquatic Ecosystems. Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-76-001. 64 pp.

IJC. 1981. Annual Report. Report to the Great Lakes Water Quality Board/Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

Jensen, S. and R. Rosenberg. 1975. Degradability of some chlorinated aliphatic hydrocarbons in seawater and sterilized water. Water Res. 9: 659-661.

Kaiser, K.L.E. and I. Valdmanis. 1979. Volatile chloro- and chlorofluorocarbons in Lake Erie – 1977 and 1978. J. Great Lakes Res. 5: 160-169.

Kaiser, K.L.E., M.E. Comba and H. Huneault. 1983. Volatile halocarbon contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Res. 9: 212-223.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

McConnell, G., D.M. Ferguson and C.R. Pearson. 1975. Chlorinated hydrocarbons and the environment. Endeavor 34: 13-18.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B 189: 305-322.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003. 147 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6: 1-77.

U.S. EPA. 1974. Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride (appendices). Report on the Activities and Findings of the Vinyl Chloride Task Force, U.S. Environmental Protection Agency, Washington, D.C. 67 pp.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency, Washington, D.C. Contract No. 68-01-4646.

U.S. EPA. 1979. Chloroethene. 1,1-Dichloroethene. 1,2-Dichloroethene. Trichloroethene. Tetrachloroethene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 49-1 to 49-10, 50-1 to 50-10, 51-1 to 51-10, 52-1 to 52-13, and 53-1 to 53-13.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Trichloroethylene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-077.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Dichloroethylenes. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-041.

U.S. EPA. 1980c. Ambient Water Quality Criteria for Tetrachloroethylene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-073.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Yung, Y.L., M.B. McElroy and S.C. Wofsy. 1975. Atmospheric halocarbons: A discussion with emphasis on chloroform. Geophys. Res. Lett. 2: 397-399. (Cited in U.S. EPA 1979.)

6.3.4.3 Chlorinated Propanes and Propenes

6.3.4.3.1 Uses and Production

The principal uses of dichlorinated propanes and propenes are as soil fumigants for the control of nematodes, as oil and fat solvents and in dry-cleaning and degreasing processes (Verschueren 1983; Worthing 1983). 1,2-Dichloropropane ($ClCH_2CHClCH_3$) is used as an insecticidal fumigant, and 1,3-dichloropropene ($ClCH_2CHCHCl$) is used as a soil fumigant and nematicide. Mixtures of 1,2-dichloropropane and 1,3-dichloropropene may also be used (Worthing 1983). No production of chlorinated propanes and propenes occurs in Canada. In 1981 and 1982, 1104 and 1101 t, respectively, of the formulated fumigant dichloropropene were imported into Canada (Statistics Canada 1983).

6.3.4.3.2 Sources and Pathways for Entering the Aquatic Environment

Chlorinated propanes and propenes can enter the aquatic environment as discharges from industrial effluents, as runoff from agricultural land and from municipal effluents (U.S. EPA 1980). 1,2-Dichloropropane was detected in the final effluent of various petrochemical plants discharging into the St. Clair River at a concentration range of 1-10 $\mu g \cdot L^{-1}$; *trans*-1,3-Dichloropropene was detected in one of three samples at an estimated concentration of 1-10 $\mu g \cdot L^{-1}$ (Munro *et al.* 1985). Total Ontario municipal and industrial loading of 1,2-dichloropropane to the Niagara River and its tributaries was 0.6 $g \cdot d^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981). Total gross loadings, concentration ranges and detection frequencies for 1,2-dichloropropane and 1,3-dichloropropylene in the final effluents of Cornwall, Ontario, industrial and municipal plants are presented in Table 6-75.

6.3.4.3.3 Environmental Concentrations

Chlorinated propanes and propenes were detected in New Orleans drinking water (U.S. EPA 1980). 1,2-Dichloropropane was identified in finished drinking water, surface water and industrial effluents in the United States. 1,3-Dichloropropene was also identified in finished drinking water (Shackelford and Keith 1976).

Sampling results for chlorinated propanes and propenes are not reported in NAQUADAT (1985). 1,2-Dichloropropane was detected in one of two samples taken from the St. Lawrence River at Cornwall, Ontario, at a concentration of 29.2 $\mu g \cdot L^{-1}$. 1,2-Dichloropropane and *trans*-1,3-dichloropropene were detected in Cornwall municipal drinking water in trace (5 $\mu g \cdot L^{-1}$) quantities (Environment Canada 1984). 1,2-Dichloropropane was detected in 14 of 24 samples taken from the St. Clair River at a concentration range of 10-100 $\mu g \cdot L^{-1}$. *trans*-1,3-Dichloropropene was detected in three samples from the St. Clair River at a concentration range of 1-100 $\mu g \cdot L^{-1}$ (Munro *et al.* 1985). Dichloropropane (isomer not specified) was detected in only 1 of 72 samples taken from the upper Niagara River in a 1979-1980 survey, at a concentration range of not detectable to less than 1 $ng \cdot L^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981).

Table 6-75. Total Gross Loadings, Concentration Ranges and Detection Frequencies for 1,2-Dichloropropane and 1,3-Dichloropropylene in the Final Effluents of Industrial and Municipal Plants in Cornwall, Ontario

Compound	Gross loadings ($kg \cdot d^{-1}$)	Concentration range ($\mu g \cdot L^{-1}$)	Detection frequency (%)
1,2-Dichloropropane	2.59	ND[1]-357	75
trans-1,3-Dichloropropylene	1.17	ND-76.6	49

[1] ND = not detected.

Source: Environment Canada 1984.

6.3.4.3.4 Forms and Fate in the Aquatic Environment

Chlorinated propanes and propenes are low-molecular-weight saturated or unsaturated aliphatic compounds containing one or more chlorine atoms. In general, they are water-soluble, volatile and have a slight affinity for organic matter (Table 6-76) (U.S. EPA 1979; Verschueren 1983). Volatilization plays a major role in the removal of these compounds from the water column (U.S. EPA 1979).

Small calculated P_{ow} values indicate that sorption of some chlorinated propanes and propenes to organic matter is not expected to be significant (U.S. EPA 1979). 1,3-Dichloropropene, however, when applied to soil as a fumigant, was found to sorb and persist for long periods of time (Leistra 1970; Thomason and McKenry 1973). Sorption of 1,3-dichloropropene was, in general, proportional to the organic content of the soil (Leistra 1970). Degradation, probably via base-catalyzed hydrolysis, was found to be more rapid in clay than in sandy soils (Van Dijk 1973).

Table 6-76. Physical-chemical Properties of Some Chlorinated Propanes and Propenes

Compound	Molecular weight	Boiling point (°C)	Vapour pressure (kPa) at 20°C	Water solubility ($mg \cdot L^{-1}$) at 20°C	Octanol/water partition coefficient ($\log P_{ow}$)[1]
1,2-Dichloropropane	112.99	95.4	27.9 (19.6°C) 5.6	2700	2.28
cis-1,3-Dichloropropene	110.98	104.3	3.3	2700	1.98
trans-1,3-Dichloropropene	110.98	112	3.3	2800	1.98

[1] Tute 1971; U.S. EPA 1979.

Sources: U.S. EPA 1979; Verschueren 1983; Worthing 1983.

Photolysis and oxidation of chlorinated propanes and propenes are not expected to be significant in the aquatic environment (U.S. EPA 1979). 1,3-Dichloropropene is hydrolyzed in moist soil and water, yielding chloroalkyl alcohols (Castro and Belser 1966).

Because chlorinated propanes and propenes have relatively high vapour pressures, it is expected that volatilization will be their predominant fate. A half-life of 31 min was found for *cis*- and *trans*-1,3-dichloropropene (1 $mg{\cdot}L^{-1}$) as a result of their volatilization from stirred waters. Approximately 90% loss occurred in 1.5 hours (Dilling *et al.* 1975).

1,2-Dichloropropane was found to undergo minimal biotic degradation in soil (Roberts and Stoydin 1976), although *cis*- and *trans*-1,3-dichloropropene were degraded by a *Pseudomonas* sp. isolated from soil (Belser and Castro 1971).

6.3.4.3.5 References

Belser, N.O. and C.E. Castro. 1971. Biodegradation – the metabolism of the nematocides *cis*- and *trans*-3-chloroalkyl alcohol by a bacterium isolated from soil. J. Agric. Food Chem. 19: 23-26.

Castro, C.E. and N.O. Belser. 1966. Hydrolysis of *cis*- and *trans*-1,3-dichloropropene in wet soil. J. Agric. Food Chem. 14: 69-70.

Dilling, W.L., N.B. Terfertiller and G.J. Kallos. 1975. Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethene, trichloromethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9: 833-838.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality. Canada-Ontario Review Board, Ottawa.

Leistra, M. 1970. Distribution of 1,3-dichloropropene over the phases in soil. J. Agric. Food Chem. 18: 1124-1126.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Roberts, T.R. and G. Stoydin. 1976. The degradation of (Z)- and (E)-1,3-dichloropropenes and 1,2-dichloropropane in soil. Pestic. Sci. 7: 325-335. (Cited in U.S. EPA 1979.)

Shackelford, W.M. and L.H. Keith. 1976. Frequency of Organic Compounds Identified in Water. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/4-76-062. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Thomason, I.J. and M.V. McKenry. 1973. Part 1. Movement and fate as affected by various conditions in several soils. Hilgardia 42: 393-421. (Cited in U.S. EPA 1979.)

Tute, M.S. 1971. Principles and practice of Hansch analysis: A guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6: 1-77.

U.S. EPA. 1979. 1,2-Dichloropropane. 1,3-Dichloropropene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Volume II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 54-1 to 54-5 and 55-1 to 55-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Dichloropropane and Dichloropropene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-043.

Van Dijk, H. 1973. Degradation of 1,3-dichloropropenes in soil. Agro-Ecosystems 1: 193-204.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. pp. 181, 183.

6.3.4.4 Halogenated Methanes*

6.3.4.4.1 Uses and Production

Halogenated methanes are organic compounds in which one or more of the halogens are incorporated into the methane molecule (CH_4). Trihalomethanes, such as chloroform, are considered separately. Commonly recognized halogenated methanes are listed in Table 6-77, along with production figures and uses.

Production, importation, consumption and exportation of various halogenated methanes in Canada are presented in Table 6-78.

6.3.4.4.2 Sources and Pathways for Entering the Aquatic Environment

Halogenated methanes occur in the environment both from natural sources and as a result of human activities. The oceans are believed to be the primary source of both bromo- and chloromethane (U.S. EPA 1980a); natural sources are also suggested for dichloro- and tribromomethane (NAS 1978). Substantial amounts of bromomethane also enter the environment from its extensive use as a fumigant (U.S. EPA 1980a).

The presence of many of the halomethanes in the aquatic environment is primarily a result of their use in manufacturing processes and resultant presence in industrial effluents. Others are present as a result of their use as aerosol propellants and refrigerants (U.S. EPA 1980a).

Gross loadings, concentration ranges and detection frequencies for carbon tetrachloride and methylene chloride in Cornwall municipal and industrial effluents are presented in Table 6-79. Carbon tetrachloride was detected in 34% of the 65 samples taken from the final effluents of petrochemical plants discharging into the St. Clair River, Ontario. The concentration range was estimated at 1-10 $\mu g{\cdot}L^{-1}$ (Environment Canada 1984). In the same study, methylene chloride was detected in 22% of the 65 samples at a concentration range of 10-100 $\mu g{\cdot}L^{-1}$. Trichlorofluoromethane was not detected in any of 15 samples taken from the final effluents of the same petrochemical plants (Munro *et al.* 1985). Total municipal and industrial loadings for carbon tetrachloride and methylene chloride to the Niagara River and its tributaries were estimated at not detectable and 5.979 $kg{\cdot}d^{-1}$, respectively (Environment Canada/Ontario Ministry of the Environment 1981).

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* Excluding trihalomethanes (see Section 6.3.4.7).

Table 6-77. Common Halogenated Methanes and Their Uses

Compound	Uses
Chloromethane (methyl chloride)	Herbicide, refrigerant, aerosol propellant, manufacture of synthetic rubber, tetraethyllead
Dichloromethane (methylene chloride)	In insecticides, fumigants
Tetrachloromethane (carbon tetrachloride)	Refrigerant, aerosol, fire-resistant chemicals, industrial solvent, fumigant
Bromomethane (methyl bromide)	Fumigant, fire-resistant chemicals, refrigerant, insecticide
Dibromomethane (methylene bromide)	Solvent and chemical intermediate
Dichlorodifluoromethane (Freon-12)	Refrigerants, solvents, aerosol propellants, fire-resistant chemicals, blowing agent for foam insulation
Trichlorofluoromethane (Freon-11)	Refrigerants, solvents, aerosol propellants, fire-resistant chemicals, blowing agent for foam insulation

Sources: NAS 1977; U.S. EPA 1980a, b.

Table 6-79. Gross Loadings, Concentration Ranges and Detection Frequencies for Carbon Tetrachloride and Methylene Chloride in Cornwall Municipal and Industrial Effluents

Compound	Gross loadings ($kg \cdot d^{-1}$)	Concentration range ($\mu g \cdot L^{-1}$)	Detection frequency (%)
Carbon tetrachloride (tetrachloromethane)	42.1	ND[1]-45 500	31
Methylene chloride (dichloromethane)	10.9	ND-331	41

[1] ND = not detected.

Source: Environment Canada 1984.

6.3.4.4.3 Environmental Concentrations

Carbon tetrachloride was detected in two of four samples taken from the St. Lawrence River at Cornwall, Ontario, at concentrations ranging from 5 to 16 600 $\mu g \cdot L^{-1}$. Methylene chloride was also detected in both samples from the St. Lawrence River at concentrations ranging from 5 to 23.9 $\mu g \cdot L^{-1}$. Carbon tetrachloride was found in Cornwall municipal drinking water at a concentration of 5 $\mu g \cdot L^{-1}$; methylene chloride was also detected, but the concentration was not measured (Environment Canada 1984). Carbon tetrachloride was detected in 24 samples taken from the St. Clair River at concentrations ranging from 1 to 10 $\mu g \cdot L^{-1}$; another three samples had concentrations ranging from 10 to 100 $\mu g \cdot L^{-1}$. Methylene chloride was detected in the surface waters of the St. Clair River in two samples at concentrations ranging from 10 to 100 $\mu g \cdot L^{-1}$; trichlorofluoromethane was detected in only one of nine samples at a concentration between 1 and 10 $\mu g \cdot L^{-1}$ (Munro *et al.* 1985).

Several volatile halogenated compounds were identified in Lake Erie water during a sampling study in 1978. Mean concentrations (standard deviations) for chloroform and carbon tetrachloride were 15 ± 4 and 19 ± 11 $ng \cdot L^{-1}$, respectively. Dichlorodifluoromethane (Freon 12) and trichlorofluoromethane (Freon 11) were found in concentrations of 76 ± 12 and 34 ± 26 $ng \cdot L^{-1}$, respectively (Kaiser and Valdmanis 1979).

Table 6-78. Production, Consumption, Importation and Exportation of Fluorochloromethanes, Carbon Tetrachloride, Methylene Chloride and Methyl Chloride, and Importation of Other Halogenated Methanes in Canada

Compound	Year	Production (t)	Consumption (t)	Importation (t)	Exportation (t)
Fluorochloromethanes	1983	16 000	14 900	500	0
(trichlorofluoromethane, dichlorodifluoromethane and chlorodifluoromethane)	1984	16 400	15 400	500	0
Carbon tetrachloride	1983	15 000	15 100	1 000	100
(tetrachloromethane)	1984	15 000	15 500	500	0
Methylene chloride	1983	0	11 600	11 900	0
(dichloromethane)	1984	0	12 000	12 000	0
Methyl chloride	1983	0	4 000	4 000	0
(chloromethane)	1984	0	5 650	5 700	0
Bromotrifluoromethane	1981			107	
	1982			162	
Chlorotrifluoromethane	1981			27	
	1982			18	
Chlorofluoromethanes	1981			10	
(group not specified)	1982			23	
Bromomethane	1981			32	
(methyl bromide), formulated fumigant	1982			71	

Sources: Statistics Canada 1983; CORPUS Information Services 1984.

Table 6-80. Concentration Ranges of Methylene Chloride in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water During 1979 and 1980

Location	Year	Total number of samples	Number of detectable samples	Concentration range ($\mu g \cdot L^{-1}$)
Niagara-on-the-Lake	1979	9	5	ND[1]-9.0
	1980	14	11	ND-2.1
Niagara Falls	1979	9	6	ND-4.0
	1980	13	12	ND-39.5
Fort Erie	1979	9	7	ND-3.0
	1980	14	12	ND-10.2
St. Catharines	1980	8	8	<0.001-1.2

[1] ND = not detected.

Source: Environment Canada/Ontario Ministry of the Environment 1981.

Ninety-five stations were sampled in Lake Ontario in 1981 for volatile halocarbons. Lake-wide means (standard deviations) were reported for several compounds: methylene chloride, 572 ± 826 $ng \cdot L^{-1}$; trichlorofluoromethane, 249 ± 882 $ng \cdot L^{-1}$; chloroform, 18 ± 92 $ng \cdot L^{-1}$ and bromodichloromethane, 3 ± 9 $ng \cdot L^{-1}$. In a 16-station survey of the Lower Niagara River, chloroform was measured with a mean concentration of 22 ± 32 $ng \cdot L^{-1}$. Numerous other halogenated methanes, ethanes and ethylenes were identified (Kaiser *et al.* 1983). In addition, numerous compounds were identified in 1980-1981 in the Welland River, a tributary to the Niagara River (Kaiser and Comba 1983).

The concentration ranges of methylene chloride in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-80. Carbon tetrachloride was detected in 2 of 76 samples taken from the upper Niagara River at concentrations ranging from not detectable to 12 $ng \cdot L^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.4.4.4 Forms and Fate in the Aquatic Environment

Halogenated methanes are single-carbon compounds in which one or more of the hydrogen atoms of the methane parent molecule are substituted with fluorine, chlorine, bromine or iodine. Halomethanes include mono-, di-, tri- and tetrahalomethanes. Trihalomethanes are considered in a separate profile (see Section 6.3.4.7). Some physical-chemical properties of halomethanes appear in Table 6-81. In general, halomethanes are either gases or low-boiling liquids at ambient temperatures, and are water-soluble and volatile.

Sorption to surfaces is not considered to be an important process in the aquatic environment; few data, however, are available. Several halomethanes have octanol/water partition coefficients in the range of 10^2, indicating the possibility for uptake by lipophilic material (Hansch *et al.* 1975). Dichloromethane did not significantly bind to either inorganic or organic material (Dilling *et al.* 1975). Coarse gravels had little adsorptive capacity for tetrachloromethane; however, sediments rich in organic detritus had a significant adsorptive capacity (Pearson and McConnell 1975). No information is available for other halomethanes (U.S. EPA 1979).

Photolysis in the water column is not considered to be significant (Dilling *et al.* 1975). Likewise, oxidation and hydrolysis are not expected to be important (Radding *et al.* 1977; Mabey and Mill 1978).

Volatilization appears to be the primary process for the removal of halomethanes from the water column. Evaporative half-lives for 1 $mg \cdot L^{-1}$ aqueous solutions of chloromethane, dichloromethane and tetrachloromethane were found to be less than 0.5 h (Dilling 1977). Although no specific data are available, it is expected that other halomethanes also readily volatilize (U.S. EPA 1979). Once in the troposphere, photooxidation takes place, resulting in half-lives of 0.37 (Cox *et al.* 1976) to 0.89 (Yung *et al.* 1975) years for chloromethane, 0.3 years for dichloromethane (Cox *et al.* 1976) and 1 year for bromomethane (Wofsy *et al.* 1975). Tetrachloromethane, trichlorofluoromethane and dichlorodifluoromethane are stable

Table 6-81. Physical-chemical Properties of Some Halomethanes

Compound	Alternate names	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa) at 20°C	Water solubility ($mg \cdot L^{-1}$) at 25°C	Octanol/water partition coefficient (log P_{ow})
Chloromethane	Methyl chloride	CH_3Cl	50.59	−97.73	−24.2	502[1]	6 450[2] (20°C) 7 250[4] (20°C)	0.91[3]
Dichloromethane	Methylene chloride	CH_2Cl_2	84.94	−95	39.75	48[4]	13 200[4] 20 000[2]	1.25[3]
Tetrachloromethane	Carbon tetrachloride	CCl_4	153.82	−22.9	76.54	12[4]	785[4] (20°C)	2.64[3]
Bromomethane	Methyl bromide	CH_3Br	94.94	−93.6	4.6	189[5]	900[6] (20°C)	1.1[7]
Dibromomethane	Methylene bromide	CH_2Br_2	173.86	−52.8	98.2	453	12[8] (20°C)	1.54[9]
Dichlorodifluoromethane	Freon-12	CCl_2F_2	129.91	−158	−29.8	573[4]	280[4]	2.16[3]
Trichlorofluoromethane	Freon-11	CCl_3F	137.4	−111	23.8	89[4]	1 110[4] (20°C)	2.53[3]

[1] McConnell *et al.* 1975.
[2] Dean 1973.
[3] Hansch *et al.* 1975.
[4] Pearson and McConnell 1975.
[5] U.S. EPA 1976.
[6] Verschueren 1983.
[7] Tute 1971.
[8] Clayton and Clayton 1981.
[9] Lyman *et al.* 1982.

Sources: U.S. EPA 1979; Verschueren 1983.

in the troposphere, with half-lives ranging from several to several hundred years (Howard and Durkin 1973; Cox *et al.* 1976; Jesson *et al.* 1977; Hanst 1978).

Little information is available on the biodegradation of halomethanes. Tetrachloromethane did not degrade in a standard biological oxygen demand bottle test (Pearson and McConnell 1975). Dichlorodifluoromethane was found to be persistent in natural waters (Su and Goldberg 1976). Little information is available on uptake by aquatic organisms. Tetrachloromethane (calculated log P_{ow} 2.64) (Hansch *et al.* 1975) would be expected to concentrate under conditions of continuous exposure; however, biomagnification is unlikely (Pearson and McConnell 1975). A bioconcentration factor of 30 was found for exposure of bluegills (*Lepomis macrochirus*) to tetrachloromethane for 21 d (U.S. EPA 1978, 1980b). Dichlorodifluoromethane and trichlorofluoromethane show little tendency to accumulate (Howard *et al.* 1975); however, residues of 0.1-5 $\mu g \cdot kg^{-1}$ (dry weight) of trichlorofluoromethane have been found in various organs of marine fish and molluscs (Dickson and Riley 1976).

6.3.4.4.5 References

Clayton, G.D. and F.E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology. 3rd edition. John Wiley & Sons, New York. 2878 pp.

CORPUS Information Services. 1984. Fluorochloromethane. Carbon tetrachloride. Methylene chloride. Methyl chloride. CPI Product Profiles. Don Mills, Ontario.

Cox, R.A., R.G. Derwent, A.E.J. Eggleton and J.E. Lovelock. 1976. Photochemical oxidation of halocarbons in the troposphere. Atmos. Environ. 10: 305-308.

Dean, J.A. (ed.). 1973. Lange's Handbook of Chemistry. 11th edition. McGraw-Hill Book Co., New York. 1576 pp. (Cited in U.S. EPA 1979.)

Dickson, A.G. and J.P. Riley. 1976. The distribution of short-chain halogenated aliphatic hydrocarbons in some marine organisms. Mar. Pollut. Bull. 7: 167-169. (Cited in U.S. EPA 1979.)

Dilling, W.L. 1977. Interphase transfer processes. II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11: 405-409.

Dilling, W.L., N.B. Tefertiller and G.J. Kallos. 1975. Evaporation rates of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9: 833-838.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality. Canada-Ontario Review Board, Ottawa.

Hansch, C., A. Vittoria, C. Silipo and P.Y.C. Jow. 1975. Partition coefficients and the structure-activity relationship of the anesthetic gases. J. Med. Chem. 18: 546-548.

Hanst, P.L. 1978. Halogenated pollutants. Part II. Noxious trace gases in the air. Chemistry 51: 6-12.

Howard, P.H. and P.R. Durkin. 1973. Preliminary Environmental Hazard Assessment of Chlorinated Naphthalenes, Silicones, Fluorocarbons, Benzenepolycarboxylates and Chlorophenols. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/2-74-001. 263 pp.

Howard, P.H., P.R. Durkin and A. Handrett. 1975. Environmental Hazard Assessment of One and Two Carbon Fluorocarbons. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/2-75-003. 246 pp.

Jesson, J.P., P. Meakin and L.C. Glasgow. 1977. The fluorocarbon-ozone theory. II. Tropospheric lifetime – an estimate of tropospheric lifetime of CCl_3F. Atmos. Environ. 11: 499-508.

Kaiser, K.L.E. and M.E. Comba. 1983. Volatile contaminants in the Welland River Watershed. J. Great Lakes Res. 9: 274-280.

Kaiser, K.L.E. and I. Valdmanis. 1979. Volatile chloro- and chlorofluorocarbons in Lake Erie – 1977 and 1978. J. Great Lakes Res. 5: 160-169.

Kaiser, K.L.E., M.E. Comba and H. Huneault. 1983. Volatile halocarbon contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Res. 9: 212-223.

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt (eds.). 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill Book Co., New York. pp. 1-1 to 1-54.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7: 383-415.

McConnell, G., D.M. Ferguson and C.R. Pearson. 1975. Chlorinated hydrocarbons and the environment. Endeavor 34: 13-18.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences. U.S. National Research Council, Washington, D.C. 939 pp.

NAS. 1978. Nonfluorinated Halomethanes in the Environment. National Academy of Sciences. U.S. National Research Council, Washington, D.C. (Cited in U.S. EPA 1980a.)

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B 189: 305-332.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003. 147 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Su, C. and E.D. Goldberg. 1976. Environmental concentrations and fluxes of some halocarbons. *In* Marine Pollutant Transfer. H.L. Windom and R.A. Duce (eds.). Lexington Books, D.C. Heath and Co., Lexington, Massachusetts. pp. 353-374. (Cited in U.S. EPA 1979.)

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug. Res. 6: 1-77.

U.S. EPA. 1976. A Literature Survey Oriented Towards Adverse Environmental Effects Resultant from the Use of Azo Compounds, Brominated Hydrocarbons, EDTA, Formaldehyde Resins, and *o*-Nitrochlorobenzene. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/2-76-005. 480 pp.

U.S. EPA. 1978. In-depth Study of Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency, Cincinnati, Ohio. Contract No. 68-01-4646.

U.S. EPA. 1979. Chloromethane. Dichloromethane. Tetrachloromethane. Bromomethane. Dichlorodifluoromethane. Trichlorofluoromethane. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 38-1 to 38-9, 39-1 to 39-11, 41-1 to 41-10, 58-1 to 58-7, 62-1 to 62-8 and 63-1 to 63-8.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Halomethanes. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-051.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Carbon Tetrachloride. Office of Water Regulation and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-026.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Wofsy, S.C., M.B. McElroy and Y.L. Yung. 1975. The chemistry of atmospheric bromine. Geophys. Res. Lett. 2: 215-218.

Yung, Y.L., M.B. McElroy and S.C. Wofsy. 1975. Atmospheric halocarbons: a discussion with emphasis on chloroform. Geophys. Res. Lett. 2: 397-399.

6.3.4.5 Hexachlorobutadiene

6.3.4.5.1 Uses and Production

Hexachloro-1,3-butadiene, or hexachlorobutadiene (HCBD), is a by-product of chemical industries that produce chlorinated hydrocarbons, such as tetrachloroethylene, trichloroethylene and carbon tetrachloride. It is used in the chemical industry primarily as a solvent for many organic substances, particularly elastomers. It is especially useful in recovering chlorine from waste gases and in manufacturing rubber compounds, lubricants and hydraulic fluids. It is also used as a heat transfer fluid in electrical transformers (U.S. EPA 1980; Environment Canada 1983). Actual Canadian usage of hexachlorobutadiene is unknown (Environment Canada 1983).

Importation figures for hexachlorobutadiene in 1981 and 1982 are unavailable, because the compound does not have a separate category in the Statistics Canada (1983) publication. This may indicate that importation quantities for hexachlorobutadiene are not large.

In 1979, the Canadian output of HCBD as a by-product of carbon tetrachloride, trichloroethylene and tetrachloroethylene production was estimated to be between 160 and 340 t, primarily limited to sites on the lower Great Lakes and St. Lawrence River where these three chemicals are manufactured (Environment Canada 1983). Hexachlorobutadiene is not known to be produced in Canada (Environment Canada 1980).

In June, 1984, hexachlorobutadiene was deleted from the Environmental Contaminants Act List of Priority Chemicals. The rationale was that the potential exposure of humans and the ecosystem was not sufficient to merit further investigation based on the commercial use patterns and data on environmental concentrations (Environment Canada 1985).

6.3.4.5.2 Sources and Pathways for Entering the Aquatic Environment

The presence of HCBD in the environment results from anthropogenic sources. It occurs as a tarry by-product; volatilization and solubilization from this waste are the primary mechanisms for dispersal into and throughout the environment. Waste holding areas are the most significant emission sources. Wastewater from industrial processes may also be a significant source of contamination (Li *et al*. 1976).

HCBD was found at 5 of 31 sites and in 5 of 88 samples during a survey of the aqueous effluent from petrochemical plants along the St. Clair River. In four of these effluents, the HCBD concentration was estimated to be between 10 and 100 $\mu g \cdot L^{-1}$, whereas in the fifth it was estimated to be between 0.05 and 0.1 $\mu g \cdot L^{-1}$ (Bonner and Meresz 1981). In another survey of the petrochemical plant effluents in 1979 and 1980, hexachlorobutadiene was detected (detection limit 1 $\mu g \cdot L^{-1}$) in 6 of 16 samples. Only three of the detectable samples were estimated at concentrations ranging from 1 to 100 $\mu g \cdot L^{-1}$ (Munro *et al*. 1985).

In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of hexachlorobutadiene were observed in 13 samples (Environment Canada 1984).

Details of the movement of HCBD in the environment are generally unknown, but it has been detected in the atmosphere (range 0.003-460 $\mu g \cdot m^{-3}$) in the vicinity of chemical plants where HCBD is a known by-product (Li *et al*. 1976).

6.3.4.5.3 Environmental Concentrations

The HCBD content of waters is highly variable, and apparently depends on the level of industrial activity. In Canada, monitoring has been concentrated on the Great Lakes system (Environment Canada 1983). HCBD was not detected (detection limit 0.05-0.1 $\mu g \cdot L^{-1}$) in the St. Clair River; however, it was detected in the river sediments at one of the three sites examined at approximately 50 $mg \cdot kg^{-1}$ (wet weight) (Bonner and Meresz 1981). HCBD was detected (detection limit 1 $\mu g \cdot L^{-1}$) in five of seven samples taken from the St. Clair River in 1979; the concentrations, however, were not measured (Munro *et al*. 1985). Sampling results for hexachlorobutadiene are not reported in NAQUADAT (1985). Five freshwater fish species (lake trout, lake herring, longnose sucker, American smelt and walleye) from Lake Superior contained 0.5-1.0 $mg \cdot kg^{-1}$ (essentially at the detection limit). Occurrence of HCBD was sporadic, with less than 1% of the more than 10 000 fish examined having HCBD present (Swain 1978; Swain *et al*. 1978). Levels ranging from 1.7 to 2.5 $mg \cdot kg^{-1}$ were detected in fish from Lake Ontario (Kuehl *et al*. 1981). The mean concentration of HCBD in Lake Ontario fish was found to be 0.2 ± 0.08 $ng \cdot g^{-1}$ (Oliver and Niimi 1983).

6.3.4.5.4 Forms and Fate in the Aquatic Environment

Hexachloro-1,3-butadiene (molecular weight 260.76, melting point −21°C, boiling point 215°C) (U.S. EPA 1979; Verschueren 1983; Environment Canada 1983) has a water solubility of 2 $mg \cdot L^{-1}$ at 20°C and a vapour pressure of 20 Pa at 20°C (Pearson and McConnell 1975). Hexachlorobutadiene has a calculated log octanol/water partition coefficient of 3.74 (Tute 1971). Sorption to sediments is considered to be an important mechanism for its removal from the water column; little information is available on other transport or removal processes (U.S. EPA 1979).

Photolysis, oxidation and hydrolysis are not expected to be significant removal mechanisms for hexachlorobutadiene in the aquatic environment (U.S. EPA 1979). Unlike other short-chain, halogenated aliphatic compounds, hexachlorobutadiene has a lower vapour pressure, indicating a relatively low potential for volatilization (U.S. EPA 1979).

No information was found on the biodegradation of hexachlorobutadiene in the aquatic environment (U.S. EPA 1979). Concentration factors in algae and animals, measured in the laboratory and in the field, were found to be generally below 300 for short-term exposures (U.S. EPA 1979). Bioconcentration factors for goldfish (*Carassius auratus*) ranged from 920 to 2300 upon exposure to hexachlorobutadiene for 49 d (U.S. EPA 1976). Bioconcentration factors of 160 for algae (*Oedogonium cardiacum*) (7-d exposure), 60 for crayfish (*Procambarus clarki*) (10-d exposure) and 29 for largemouth bass (*Micropterus salmoides*) (10-d exposure) were recorded (Leeuwangh *et al.* 1975). HCBD exposure (<1 ng·L^{-1}) to rainbow trout (*Salmo gairdneri*) resulted in a mean bioconcentration factor of 5800 ± 840 (Oliver and Niimi 1983). Biomagnification in an aquatic food chain has not been demonstrated (Environment Canada 1984).

6.3.4.5.5 References

Bonner, R.F. and O. Meresz. 1981. St. Clair River Organics Study. Identification and Quantification of Organic Compounds. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario. (Cited in Environment Canada 1983.)

Environment Canada. 1980. INFONOTES: Hexachlorobutadiene. Environmental Protection Service, Ottawa.

Environment Canada. 1983. Hexachlorobutadiene. *In* Guidelines for Surface Water Quality. Vol. 2. Organic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada. 1985. Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa.

Kuehl, D.W., K.L. Johnson, B.C. Butterworth, E.N. Leonard and G.D. Veith. 1981. Quantification of octachlorostyrene and related compounds in Great Lakes fish by gas chromatography – mass spectrometry. J. Great Lakes Res. 7: 330-335.

Leeuwangh, P., H. Bult and L. Schneiders. 1975. Toxicity of hexachlorobutadiene in aquatic organisms. *In* Sublethal Effects of Toxic Chemicals on Aquatic Animals. Proc. Swedish-Netherlands Symp. J.H. Koeman and J.J. Strik (eds.). Wageningen, The Netherlands. (Cited in Environment Canada 1983.)

Li, R.T., J.E. Going and J.L. Spigarelli. 1976. Sampling and Analysis of Selected Toxic Substances. Task IB. Hexachlorobutadiene. U.S. Environmental Protection Agency, Washington, D.C. EPA-560/6-76-015.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Oliver, B.G. and A.J. Niimi. 1983. Bioconcentration of chlorobenzenes from water by rainbow trout: correlations with partition coefficients and environmental residues. Environ. Sci. Technol. 17: 287-291.

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B 189: 305-332.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Swain, W.R. 1978. Chlorinated organic residues in fish, water and precipitation from the vicinity of Isle Royale, Lake Superior. J. Great Lakes Res. 4: 398-407.

Swain, W.R., R. Wilson, N. Nen and G. Porter. 1978. Persistent organic and heavy metal residues in Lake Superior fish. Ecological Research Series. U.S. Environmental Protection Agency. (Personal communication of data from the senior author.) (Cited in Environment Canada 1983.)

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug. Res. 6: 1-77.

U.S. EPA. 1976. An Ecological Study of Hexachlorobutadiene. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA 560/6-76-010.

U.S. EPA. 1979. Hexachlorobutadiene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Volume II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 56-1 to 56-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Hexachlorobutadiene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-053.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.4.6 Hexachlorocyclopentadiene

6.3.4.6.1 Uses and Production

Hexachlorocyclopentadiene is a chemical intermediate used in the production of organochlorine pesticides and in fire-retardant substances. Other uses include the manufacturing of dyes, pharmaceuticals, resins and germicides. The pesticide products of hexachlorocyclopentadiene registered for use in Canada include aldrin, isodrin, chlordane, heptachlor, endrin, chlordecone (Kepone), endosulfan, dienochlor (Pentac) and dieldrin (Agriculture Canada 1985). Various dechlorane (Mirex) products are used as fire retardants (U.S. EPA 1980; Gilbertson 1982). Most of the hexachlorocyclopentadiene-based pesticides in the U.S.A. have been banned or severely restricted (U.S. EPA 1980).

The flame retardant, dechlorane, is not manufactured in Canada, and only two companies in the U.S.A. produce it. Dechlorane's uses include the manufacturing of fire-retardant rubber, polypropylene, polyethylene, polymeric and epoxy resins, nylon, flexible wire sheathing, extreme pressure lubricants, rigid polyurethane foams, unsaturated polyesters and automobile sealants (Gilbertson 1982).

In 1978, the annual production of dechlorane in the U.S.A. was estimated at 25 000 t (Bell *et al.* 1978). The latest available data report that between 1966 and 1977, approximately 200 t of Dechlorane Plus were imported into Canada (Gilbertson 1982). Canadian importation data on six of the nine organochlorine pesticides and one fire retardant which use hexachlorocyclopentadiene as a chemical intermediate in their production are presented in Table 6-82. No importation data are available on hexachlorocyclopentadiene, but 173 and 167 t of its salt, chlorendic acid, were imported in 1983 and 1984, respectively (Statistics Canada 1985).

As of June, 1984, dechlorane was removed from the Environmental Contaminants Act List of Priority Chemicals because its use patterns and data on environmental concentrations had led to the conclusion that the potential exposure of humans and the ecosystem was not sufficient to merit further in-depth investigation at this time (Environment Canada 1985).

6.3.4.6.2 Sources and Pathways for Entering the Aquatic Environment

Hexachlorocyclopentadiene enters the environment from industrial discharges, emissions from pesticides and fire retardant manufacturing. Discharges of hexachlorocyclopentadiene are small. However, hexachlorocyclopentadiene may occasionally enter the environment through pesticide use if

Table 6-82. Importation[1] of Aldrin, Chlordane, Endosulfan, Isodrin, Chlordecone, Pentac and Dechlorane into Canada

Compound	Amount (t)	
	1981	1982
Aldrin	0	0
Chlordane	43	27
Endosulfan, isodrin and chlordecone	—[2]	—[2]
Pentac (dienochlor)	4	5
Dechlorane (fire retardant)	8	14

[1] Refer to the separate parameter sections for endrin, heptachlor and dieldrin for their respective importation data.

[2] Not reported in a separate category in Statistics Canada, but are grouped in a category with many other pesticides. This is an indication that importation is low for these pesticides.

Source: Statistics Canada 1983.

present as an impurity in hexachlorocyclopentadiene-based pesticides because of its role as a chemical intermediate. Landfill sites are a potential source of dechloranes through discarded plastic products (U.S. EPA 1980).

6.3.4.6.3 Environmental Concentrations

Dechlorane Plus at concentrations as high as 100 $\mu g \cdot L^{-1}$ has been detected in water samples from the Credit River in southern Ontario. In the same area, landfill seepage contained 0.6 $mg \cdot L^{-1}$. It was estimated that about 1.5 kg of hexachlorocyclopentadiene were entering this system per year. Another landfill site near the Speed River in Ontario was estimated to be releasing about 1 g of hexachlorocyclopentadiene per year to the system; concentrations in the seepage reached 89 $\mu g \cdot L^{-1}$ (Gilbertson 1982). Sampling results for hexachlorocyclopentadiene are not reported in NAQUADAT (1985). In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of hexachlorocyclopentadiene were observed in 13 samples (Environment Canada 1984).

6.3.4.6.4 Forms and Fate in the Aquatic Environment

Hexachlorocyclopentadiene, or 1,2,3,4,5,5-hexachlorocyclopentadiene [molecular weight 272.77, boiling point 239°C (U.S. EPA 1979; Verschueren 1983)] has a water solubility of 1.8 $mg \cdot L^{-1}$ at 25°C (Zepp *et al.* 1979) and a vapour pressure of 11 Pa at 25°C (Ungnade and McBee 1957). Since it is highly photoreactive, photolysis is expected to be the primary removal mechanism in the aquatic environment. Hydrolysis, sorption and bioaccumulation may also play significant roles in the removal of hexachlorocyclopentadiene under specific environmental conditions (U.S. EPA 1979).

Hexachlorocyclopentadiene has a calculated log octanol/water partition coefficient of 3.99 (Zepp *et al.* 1979), and, hence, sorption to organic-rich sediments is expected to occur. Compared with other processes, however, sorption is considered to be relatively insignificant (U.S. EPA 1979).

Both direct and indirect photolysis appear to be important in the removal of hexachlorocyclopentadiene from the water column. Photolytic half-lives of approximately 10 min have been recorded (Zepp *et al.* 1979).

Although little environmentally relevant information is available, chemical oxidation and volatilization are not expected to be important (Zepp *et al.* 1979). Hydrolytic half-lives of 14 d at 25°C were found to be independent of pH in the range of pH 5 to 9 (Zepp *et al.* 1979).

Biodegradation is probably not an important removal mechanism in the aquatic environment (Zepp *et al.* 1979). In a model ecosystem study, degradation by algae, snails, mosquito larvae and fish was relatively minor (Lu *et al.* 1975). In the same model study, bioaccumulation of hexachlorocyclopentadiene did occur (concentration factors of 340 for algae, 929 for snail, 1634 for mosquito larvae and 448 for fish) (Lu *et al.* 1975). Juvenile fathead minnows (*Pimephales promelas*) in Lake Superior water (temperature 25 ± 2°C; dissolved oxygen 7.2-8.6 $mg \cdot L^{-1}$; alkalinity 42-43 $mg \cdot L^{-1}$ as $CaCO_3$; pH 7.2-7.7) exposed to hexachlorocyclopentadiene in a flow-through system for 30 d had a bioconcentration factor below 11 (Spehar *et al.* 1979). A half-life of 9 d was determined for hexachlorocyclopentadiene in goldfish (*Carassius auratus*) (Podowski and Khan 1984).

6.3.4.6.5 References

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Bell, M.A., R.A. Ewing and G.A. Lutz. 1978. Reviews of the Environmental Effects of Pollutants: XI. Hexachlorocyclopentadiene. Battelle Columbus Lab., for U.S. Environmental Protection Agency, Health Effects Research Laboratory, Cincinnati, Ohio. EPA-600/1-78-047. (Cited in U.S. EPA 1980.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada. 1985. Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa.

Gilbertson, M. 1982. A Review of Hexachlorocyclopentadiene Adducts Intended for Use as Flame Retardants. Environmental Protection Service, Environment Canada, Ottawa. Economic and Technical Review Report EPS-3-EC-82-4. 35 pp.

Lu, P.-Y., R.L. Metcalf, A.S. Hirwe and J.W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordane, heptachlor and heptachlor epoxide in a laboratory model ecosystem. J. Agric. Food Chem. 23: 967-973.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Podowski, A.A. and M.A.Q. Khan. 1984. Fate of hexachlorocyclopentadiene in water and goldfish. Arch. Environ. Contam. Toxicol. 13: 471-481.

Spehar, R.L., G.D. Veith, D.L. DeFoe and B.V. Bergstedt. 1979. Toxicity and bioaccumulation of hexachlorocyclopentadiene, hexachloronorbornadiene, and heptachloronorbornene in larval and early juvenile fathead minnows, *Pimephales promelas*. Bull. Environ. Contam. Toxicol. 21: 576-583.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1985. Imports: Merchandise Trade, Commodity Detail 1984. Catalogue No. 65-207.

Ungnade, H.E. and E.T. McBee. 1957. The chemistry of perchlorocyclopentenes and cyclopentadienes. Chem. Rev. 58: 249-320. (Cited in U.S. EPA 1979.)

U.S. EPA. 1979. Hexachlorocyclopentadiene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 57-1 to 57-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Hexachlorocyclopentadiene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-055.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Zepp, R.G., N.L. Wolfe, G.L. Baughman, P.F. Schlotzhauer and J.N. MacAllister. 1979. Dynamics of Processes Influencing the Behavior of Hexachlorocyclopentadiene in the Aquatic Environment. U.S. Environmental Protection Agency, Athens, Georgia. (Paper presented before the Division of Environmental Chemistry, American Chemical Society, September 9-14, Washington, D.C.) (Cited in U.S. EPA 1979.)

6.3.4.7 Trihalomethanes

6.3.4.7.1 Uses and Production

Trihalomethanes are halogen-substituted methane compounds with the general formula CHX_3, where X_3 may be combinations of fluorine, chlorine, bromine or iodine. Trihalomethanes include compounds such as trichloromethane ($CHCl_3$, chloroform), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and tribromomethane ($CHBr_3$, bromoform). Chloroform is the most commonly encountered trihalomethane. It is used in the production of refrigerants, plastics and pharmaceuticals, as well as in the production of aerosol propellants. It is also important as a solvent and degreasing agent. Other more minor uses include those as a linament, in cough medicines, cosmetics and fumigants. Its use as an anesthetic has been virtually stopped with the advent of new chemicals (U.S. EPA 1980). Bromoform (tribromomethane) is used in pharmaceuticals, solvents and fire-resistant materials (NAS 1978).

Chloroform has not been produced in Canada since 1976, when only 300 t were manufactured in Quebec. In each of 1983 and 1984, it was estimated that 4500 t of chloroform were imported into Canada. Domestic consumption for 1983 and 1984 was estimated at 4450 and 4630 t, respectively (CORPUS Information Services 1984). Chlorodifluoromethane was imported into Canada in 1981 and 1982 in the amounts of 139 and 210 t, respectively. Bromoform is imported into Canada, but exact figures are unavailable (Statistics Canada 1983).

6.3.4.7.2 Sources and Pathways for Entering the Aquatic Environment

The primary source of trihalomethanes, particularly chloroform, in the aquatic environment is from the reaction of chlorine with organic chemicals in effluents and raw water. The amount of chloroform produced in this reaction is generally proportional to the organic content of the water (U.S. EPA 1980). High-level point sources have also been identified, either as industrial effluents (NAS 1978) or as accidental spills in transit (Thomas *et al.* 1979).

Gross loadings, concentration ranges and detection frequencies of three trihalomethanes in final effluents of Cornwall, Ontario, industrial and municipal plants are presented in Table 6-83. Bromoform and chloroform both had a median concentration range of 1-10 μg·L⁻¹ based on 65 samples taken in final effluents discharged to the St. Clair River in 1979. The detection frequencies for bromoform and chloroform were 38 and 39%, respectively (Munro *et al.* 1985). Total Ontario municipal and industrial loadings to the Niagara River and its tributaries for chloroform, bromoform, chlorodibromomethane and dichlorobromomethane were estimated at <0.452, 0.0001, <0.008 and <0.038 kg·d⁻¹, respectively (Environment Canada/Ontario Ministry of the Environment 1981).

Table 6-83. Gross Loadings, Concentration Ranges and Detection Frequencies of Chloroform, Bromoform and Bromodichloromethane in Cornwall Municipal and Industrial Final Effluents

Compound	Gross loadings (kg·d⁻¹)	Concentration range (μg·L⁻¹)	Detection frequency (%)
Chloroform	37.2	ND[1]-1200	41
Bromoform	0.011	ND-1	6
Bromodichloromethane	0.28	ND-53.5	84

[1] ND = not detected.

Source: Environment Canada 1984.

6.3.4.7.3 Environmental Concentrations

Twenty-six of 300 raw water supplies for drinking water tested in Ontario contained detectable amounts of chloroform, whereas treated waters from these sources had concentrations ranging from 6.0 to 159.0 μg·L⁻¹ (Smillie *et al.* 1977). A cross-Canada survey found chloroform concentrations in drinking water ranging from nondetectable up to 121.0 μg·L⁻¹ (Health and Welfare Canada 1977, 1980). Surveys of U.S. waters showed similar patterns (U.S. EPA 1980). Point sources of chloroform have resulted in environmental concentrations as high as 22 000 μg·L⁻¹ (NAS 1978). Sampling results for trihalomethanes, including chloroform, bromoform and chlorodifluoromethane, are not reported in NAQUADAT (1985).

Chloroform was detected in two of three samples taken from the St. Lawrence River at Cornwall, Ontario, at concentrations ranging from 5 to 12 μg·L⁻¹. Bromodichloromethane was detected in one of two samples taken from the St. Lawrence River at a concentration of 5 μg·L⁻¹. Chloroform and bromodichloromethane were detected in Cornwall municipal drinking water at concentrations of 322 and 12.6 μg·L⁻¹, respectively (Environment Canada 1984). Chloroform was detected in 14 of 24 samples taken from the St. Clair River in 1979 at concentrations ranging from 10 to 100 μg·L⁻¹. Dichlorobromomethane and bromoform were detected in 24 samples taken from the St. Clair River in 1979 at concentrations ranging from 1 to 10 μg·L⁻¹ (Munro *et al.* 1985). Concentration ranges of chloroform in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-84. Bromoform was not detected in any of the 72 samples taken in the same survey. Chlorodibromomethane and dichlorobromomethane were each detected in 12 of 72 samples at concentrations ranging from not detectable to 0.9 μg·L⁻¹ and not detectable to 3 μg·L⁻¹, respectively (Environment Canada/Ontario Ministry of the Environment 1981).

Table 6-84. Concentration Ranges for Chloroform in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water During 1979 and 1980

Location	Year	Total number of samples	Number of detectable samples	Concentration range ($\mu g \cdot L^{-1}$)
Niagara-on-the-Lake	1979	9	5	ND[1]-0.5
	1980	14	14	<0.001-2.4
Niagara Falls	1979	9	3	ND-0.4
	1980	13	11	ND-0.6
Fort Erie	1979	9	5	ND-0.8
	1980	14	8	ND-1.5
St. Catharines	1980	8	8	<0.001-4.5

[1] ND = not detected.

Source: Environment Canada/Ontario Ministry of the Environment 1981.

6.3.4.7.4 Forms and Fate in the Aquatic Environment

Some physical-chemical properties of trihalomethanes are presented in Table 6-85. Chloroform is the most commonly encountered trihalomethane, and, hence, most available information on environmental fate pertains to this compound. Volatilization (followed by oxidation) is the major removal process of chloroform from the water column. Although less volatile, the other trihalomethanes may also be volatilized (U.S. EPA 1979).

Sorption by organic and inorganic surfaces appears to be relatively minor in the aquatic environment (U.S. EPA 1979).

Chloroform may be readily volatilized from the water column (Jensen and Rosenberg 1975). The half-life of a 1 $mg \cdot L^{-1}$ aqueous solution of chloroform as a result of volatilization in still air at an average water depth of 6.5 cm was found to be 34.5 min at 1-2°C and 18.5-25.7 min at 20°C (Dilling 1977). Although no specific information for other trihalomethanes is available, volatilization may not be as significant because they have much lower vapour pressures relative to chloroform (U.S. EPA 1979).

Direct photolysis of chloroform in the water column is not expected (Lillian *et al.* 1975; U.S. EPA 1979). However, chloroform may be oxidized once in the atmosphere, following volatilization from the water column. Half-lives ranging from 0.19 (Cox *et al.* 1976) to 0.32 years (Yung *et al.* 1975) have been reported.

Aqueous-phase oxidation of trihalomethanes in the aquatic environment is not considered to be significant (Dilling *et al.* 1975). Hydrolytic half-lives are sufficiently long (in the order of years) (Radding *et al.* 1977; Mabey and Mill 1978) to preclude hydrolysis as an important removal process in the aquatic environment.

Very little information is available on the biodegradation of trihalomethanes in the aquatic environment. Chloroform was found to be degraded very slowly in BOD (biochemical oxygen demand) bottle tests (Pearson and McConnell 1975). Because trihalomethanes have a slight affinity for lipophilic materials (Tute 1971), some bioaccumulation may be expected under conditions of continuous exposure. Bluegills (*Lepomis macrochirus*) exposed to chloroform for 14 d had a bioconcentration factor of 6; however, the half-life of the compound in tissue was less than 1 d, indicating rapid depuration (U.S. EPA 1978).

6.3.4.7.5 References

CORPUS Information Services. 1984. Chloroform (trichloromethane). CPI Product Profiles. Don Mills, Ontario.

Cox, R.A., R.G. Derwent, A.E.J. Eggleton and J.E. Lovelock. 1976. Photochemical oxidation of halocarbons in the troposphere. Atmos. Environ. 10: 305-308.

Dilling, W.L. 1977. Interphase transfer processes. II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11: 405-409.

Dilling, W.L., N.B. Tefertiller and G.J. Kallos. 1975. Evaporation rates of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9: 833-838.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality. Canada-Ontario Review Board, Ottawa.

Health and Welfare Canada. 1977. National Survey for Halomethanes in Drinking Water. Environmental Health Directorate, Ottawa. Rep. No. 77-EHD-9.

Health and Welfare Canada. 1980. Trihalomethanes. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 645-676.

Jensen, S. and R. Rosenberg. 1975. Degradability of some chlorinated aliphatic hydrocarbons in seawater and sterilized water. Water Res. 9: 659-661.

Lillian, D., H.B. Singh, A. Appleby, L. Lobban, R. Arnts, R. Gumpert, R. Hague, J. Toomey, J. Kazazis, M. Antell, D. Hansen and B. Scott. 1975. Atmospheric fates of halogenated compounds. Environ. Sci. Technol. 9: 1042-1048.

Table 6-85. Physical-chemical Properties of Trihalomethanes

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility ($mg \cdot L^{-1}$ (°C))	Octanol/water partition coefficient (log P_{ow})
Trichloromethane	119.38	−64	62	21 (20)	8000 (20)	1.97
Bromodichloromethane	163.83	−57.1	90	6.7 (20)	—	1.88
Dibromochloromethane	208.29	<−20	119-120	2.0 (10.5)	—	2.09
Tribromomethane	252.77	6-7	149	0.7 (25)	3190 (30)	2.30
Dichloroiodomethane	210.83	—	132	—	—	—

Sources: U.S. EPA 1979; Verschueren 1983.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7: 383-415.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1978. Nonfluorinated Halomethanes in the Environment. National Academy of Sciences. U.S. National Research Council, Washington, D.C. (Cited in U.S. EPA 1980.)

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B 189: 305-322.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003.

Smillie, R.A., A.A. Nicholson, O. Meresz, W.K. Duholke and G.A.V. Rees. 1977. Organics in Ontario Drinking Waters. Part II. A Survey of Selected Water Treatment Plants. Ontario Ministry of the Environment, Toronto, Ontario. OTC. 7703. (Cited in Health and Welfare Canada 1980.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Thomas, R.F., M.A. Feige and H.J. Brass. 1979. Monitoring of Trihalomethanes and Other Purgeable Compounds in a Water Supply Vulnerable to Industrial Contamination. 178th Am. Chem. Soc. National Meeting, Division of Environmental Chemistry, American Chemical Society, Sept., Washington, D.C. Pap. No. 19. (Cited in U.S. EPA 1980.)

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6: 1-77.

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. Office of Water Supply, U.S. Environmental Protection Agency, Washington, D.C. Contract No. 68-01-4646.

U.S. EPA. 1979. Trichloromethane. Tribromomethane. Bromodichloromethane. Dibromodichloromethane. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 40-1 to 40-12, 61-1 to 61-6, 59-1 to 59-6, and 60-1 to 60-6.

U.S. EPA. 1980. Ambient Water Quality Criteria for Chloroform. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-033.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Yung, Y.L., M.B. McElroy and S.C. Wofsy. 1975. Atmospheric halocarbons: a discussion with emphasis on chloroform. Geophys. Res. Lett. 2: 397-399.

6.3.5 Halogenated Ethers

6.3.5.1 Uses and Production

Halogenated ethers are used in industrial organic synthesis, textile manufacture and pesticide manufacture. They are also used as solvents for polymerization reactions (U.S. EPA 1980a, b). In 1981, 514 t of ethers (including ether alcohols, ether phenols, alcohol peroxides and ether peroxides and their derivatives) were used in Canada by manufacturers of industrial chemicals (Statistics Canada 1984).

No information is available on Canadian production of halogenated ethers. Chloroethyl vinyl ether importation information is unavailable because it is not given a separate category in the Statistics Canada (1983) publication. Instead, it is grouped with other nonspecified acyclic ethers and derivatives, indicating that importation figures are probably not very large. One tonne of dichloroethyl ether was imported into Canada in 1982, whereas no imports were reported in 1981. In 1982, 0.17 t of dichloromethyl ether were imported into Canada, and no imports were reported for 1981. No imports were reported in 1981 or 1982 for dichloroisopropyl ether (Statistics Canada 1983).

6.3.5.2 Sources and Pathways for Entering the Aquatic Environment

Halogenated ethers may enter the aquatic environment in the discharges from industrial and manufacturing processes. Several chlorinated ethers have been identified in effluents (U.S. EPA 1980a, b). In a 1980-1981 survey of various contaminants in industrial final effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of bis(chloromethyl) ether, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, 4-chlorophenyl ether and 4-bromophenyl ether were observed in 13 samples (Environment Canada 1984). Bis(2-chloroisopropyl) ether was detected in three of five samples taken from various petrochemical plants which discharge into the St. Clair River; the concentration range was 1-10 $\mu g \cdot L^{-1}$ (Munro *et al.* 1985).

6.3.5.3 Environmental Concentrations

Chlorinated ethers have been identified in river water and finished drinking water at various locations in the United States. Concentrations, however, were usually in the nanogram to low microgram per litre concentration range (U.S. EPA 1980a, b). Bis(2-chloroisopropyl) ether was detected in one of three samples taken from the St. Clair River in 1980; the concentration, however, was not measured (Munro *et al.* 1985). Sampling results for halogenated ethers are not reported in NAQUADAT (1985).

6.3.5.4 Forms and Fate in the Aquatic Environment

Halogenated ethers are compounds that contain the R-O-R′ moiety, where R and R′ are either aliphatic or aromatic groups containing one or more halogen substituents. With few exceptions, the fate of these compounds in the aquatic environment is not well understood (U.S. EPA 1979, 1980a, b). Physical-chemical properties of some halogenated ethers appear in Table 6-86. Most of the halogenated ethers examined are relatively water-soluble, and the lower-molecular-weight compounds have relatively high vapour pressures. As may be expected, the chemical reactivities of these compounds vary widely depending upon the nature of the alkyl or aryl group and the position of the halogen substituent (U.S. EPA 1979).

Specific information is not available on the sorption of halogenated ethers by either organic or inorganic solids. With the exception of 4-chlorophenyl phenyl ether and 4-bromophenyl phenyl ether, halogenated ethers have relatively low

Table 6-86. Physical-chemical Properties of Halogenated Ethers

Compound	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility (mg·L⁻¹ (°C))	Octanol/water partition coefficient (log P_{ow})
2-Chloroethyl vinyl ether	C_4H_7OCl	106.55	—	108	3.6 (20)[1]	15 000 (25)[2]	1.28[3]
Bis(chloromethyl) ether (BCME)	$C_2H_4OCl_2$	114.96	−41.5	104	4.0 (22)[1]	22 000 (25)[2]	−0.38[4]
Bis(2-chloroethyl) ether (BCEE)	$C_4H_8OCl_2$	143.02	−46.8	178	0.1 (20)[5]	10 200 (25)[5]	1.58[3]
Bis(2-chloroisopropyl) ether (BCIE)	$C_6H_{12}OCl_2$	171.07	−97	189	0.1 (20)[5]	1 700 (25)[5]	2.58[3]
Bis(2-chloroethoxy) methane	$C_5H_{10}O_2Cl_2$	173.1	—	218.1	<0.01 (20)[1]	81 000 (25)[2]	1.26[3]
4-Chlorophenyl phenyl ether	$C_{12}H_9OCl$	203.66	−8[6]	293.03[6]	4×10^{-4} (25)[7]	3.3 (25)[7]	4.08[7]
4-Bromophenyl phenyl ether	$C_{12}H_9OBr$	249.11	18.72	310.14	2×10^{-4} (20)[1]	—	4.28[3]

[1] Dreisbach 1952.
[2] Moriguchi 1975.
[3] Leo *et al.* 1971.
[4] Radding *et al.* 1977.
[5] Verschueren 1983.
[6] Dow Chemical Company 1979.
[7] Branson 1977.

Sources: U.S. EPA 1979; Verschueren 1983.

octanol/water partition coefficients, indicating weak affinities for lipophilic materials (Leo *et al.* 1971; Branson 1977; Radding *et al.* 1977). Because of their relatively higher log octanol/water partition coefficients (P_{ow} >4), 4-chlorophenyl phenyl ether and 4-bromophenyl phenyl ether would be expected to partition to organic sediments (Leo *et al.* 1971; Branson 1977). Concentrations of 4-chlorophenyl phenyl ether were found to be fourfold higher in sediment than in water during biodegradation studies utilizing sludge (Branson 1977). Surveys of the Ohio River indicated, however, that partitioning of bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether to sediments did not occur (Kleopfer and Fairless 1972).

Photolysis and oxidation are not expected to be significant removal processes for halogenated ethers in the aquatic environment (Radding *et al.* 1977; U.S. EPA 1979). With the exception of bis(chloromethyl) ether, hydrolysis of halogenated ethers would be too slow under typical environmental conditions (Radding *et al.* 1977; U.S. EPA 1979). Bis(chloromethyl) ether (1 mg·L−1) was found to be rapidly hydrolyzed at about pH 7 and 20°C with a half-life of 38 s (Tou and Kalleo 1976).

Little information is available on either biodegradation or bioaccumulation of halogenated ethers. Activated sludge required an acclimation period of 25-30 d in order to degrade bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether (Ludzack and Ettinger 1963). In addition, no biodegradation, sorption or volatilization of either compound was observed during surveys of the Ohio River downstream from an industrial source (Kleopfer and Fairless 1972). A half-life of 4 h was found for 4-chlorophenyl phenyl ether during activated sludge treatment. However, very little degradation of 4-chlorophenyl phenyl ether was observed in experiments more closely approximating natural conditions (Branson 1978). A steady-state bioconcentration factor of 736 ± 89 for rainbow trout (*Salmo gairdneri*) muscle was recorded after 8.9 d (Branson 1977). A bioconcentration factor of 11 was found for exposure of bluegills (*Lepomis macrochirus*) to bis(2-chloroethyl) ether for 14 d (U.S. EPA 1978). Little information is available on the bioaccumulation of other halogenated ethers.

6.3.5.5 References

Branson, D.R. 1977. A new capacitor fluid – a case study in product stewardship. *In* Aquatic Toxicology and Hazard Evaluation. F.L. Meyer and J.L. Hamelink (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. ASTM Spec. Tech. Publ. 634. pp. 44-61.

Branson, D.R. 1978. Predicting the fate of chemicals in the aquatic environment from laboratory data. *In* Estimating the Hazard of Chemical Substances to Aquatic Life. J. Cairns, Jr., K.L. Dickson and A.W. Maki (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. ASTM Spec. Tech. Publ. 657. pp. 55-70.

Dow Chemical Company. 1979. Halogenated Ethers. 2020 Dow Center, Midland, Michigan. (Cited in U.S. EPA 1979.)

Dreisbach, R.R. 1952. Pressure-volume-temperature Relationships of Organic Compounds. 3rd edition. Handbook Publ., Inc., Cleveland, Ohio. 349 pp. (Cited in U.S. EPA 1979.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Kleopfer, R.D. and B.J. Fairless. 1972. Characterization of organic compounds in a municipal water supply. Environ. Sci. Technol. 6: 1036-1037.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-612.

Ludzack, F.J. and M.B. Ettinger. 1963. Biodegradability of organic chemicals isolated from rivers. Eng. Bull. Purdue Univ., Eng. Ext. Ser. 115: 278-282. (Cited in U.S. EPA 1979.)

Moriguchi, I. 1975. Quantitative structure-activity studies on parameters related to hydrophobicity. Chem. Pharm. Bull. 23: 247-257.

Munro, R.J., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003. 147 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Industrial and Agricultural Chemical Products 1982. Catalogue No. 46-224.

Tou, J.C. and G.J. Kalleo. 1976. Possible formation of bis-(chloromethyl) ether from reactions of formaldehyde and chloride ion. Anal. Chem. 48: 958-963.

U.S. EPA. 1978. In-depth Studies in Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency. Contract No. 68-01-4646.

U.S. EPA. 1979. Bis(chloromethyl) ether. Bis(2-chloroethyl) ether. Bis(2-chloroisopropyl) ether. 2-Chloroethyl vinyl ether. 4-Chlorophenyl phenyl ether. 4-Bromophenyl phenyl ether. Bis(2-chloroethoxy) methane. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 64-1 to 64-5, 65-1 to 65-7, 66-1 to 66-7, 67-1 to 67-7, 68-1 to 68-7, 69-1 to 69-7, and 70-1 to 70-7.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Haloethers. Office of Water Regulations and Standards. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-050.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Chloroalkyl Ethers. Office of Water Regulations and Standards. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-030.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.6 Monocyclic Aromatic Compounds

6.3.6.1 Benzene

6.3.6.1.1 Uses and Production

Benzene is used as an intermediate in chemical and pharmaceutical manufacturing, including the preparation of styrene, cyclohexane, detergents and pesticides. It is used as a thinner for lacquers and paints, a degreasing and cleaning agent, a solvent in the rubber industry and a fuel additive. Benzene is also used in dyes, explosives, flavours and perfumes and photographic materials (U.S. EPA 1980; Verschueren 1983).

Benzene is produced by petroleum refining, solvent recovery, coal tar distillation, coal processing and coal coking (Verschueren 1983). Benzene is produced in Canada mainly from petroleum feedstock reformation and hydrodealkylation of substituted aromatics (Environment Canada 1984a). Current Canadian production occurs in Ontario, Quebec and, since 1984, Alberta. In 1985, 556.5 × 10^3 t were produced in Canada. Importation for the same year was 43 200 t. Total domestic demand for 1984 was 434.5 × 10^3 t and exports were 165.5 × 10^3 t (CORPUS Information Services 1985).

6.3.6.1.2 Sources and Pathways for Entering the Aquatic Environment

Benzene may be released into the aquatic environment from both point and nonpoint sources. Sources include spills and releases during manufacturing, use, evaporation and combustion of fuel. Based on 1976 values, it has been estimated that (43.1-46.3) × 10^3 t·a^{-1} of benzene are released into the Canadian atmospheric environment, with approximately 85% of this total from motor vehicles (Health and Welfare Canada 1979).

In a survey during the summer of 1977 in Sarnia, Ontario, atmospheric benzene concentrations ranging from less than 1 to 28 μg·m^{-3} were found (Health and Welfare Canada 1979). In a survey of Sarnia sewage treatment plants discharging effluents into the St. Clair River, 17 of 23 plants had no detectable benzene in their effluents, whereas the remaining plant effluents contained benzene in the microgram per litre range (Duholke and Meresz 1977). Benzene was identified in 41 of 58 samples (71%) taken from eight industrial point sources and one sewage treatment plant in Cornwall, Ontario. Only three samples had concentrations above trace levels (<1-5 μg·L^{-1}) for industrial effluent; these concentrations were 64.8, 68.6 and 71.5 μg·L^{-1}, all taken from one industrial point source (Environment Canada 1984b). In a study on the variety of organic and inorganic compounds observed in the discharge of five organic chemical plants in Canada, benzene was reported in only one plant's effluent at a concentration of 0.96 μg·L^{-1} (detection limit 0.2 μg·L^{-1}) (Sigma Resource Consultants Ltd. 1985). The most recent Canadian data on atmospheric benzene emissions were reported in 1976. Total emissions into the atmosphere from Canadian sources were estimated to be between 43 355 and 46 856 t. Mobile sources accounted for between 36 793 and 38 846 t, depending on the benzene content of the various blends of gasoline, and represent over 80% of the estimated total emissions. Chemical processes using benzene and its derivatives contributed 3103 t, and surface coatings contributed a further 1790 t (Sheffield 1979).

6.3.6.1.3 Environmental Concentrations

As it is volatile, benzene will readily evaporate from surface waters; hence concentrations in the water column will generally be low (U.S. EPA 1979; Environment Canada 1984a). Benzene has been detected in water and sediment and in finished drinking water in the nanogram to microgram per litre range (Health and Welfare Canada 1979; U.S. EPA 1979). An Ontario study of 14 drinking water supplies found that benzene was present in drinking water in the nanogram per litre range at five locations (Smillie *et al.* 1977). A nationwide survey of 113 cities in the United States found that benzene was present in drinking water at seven locations, with an average concentration of 0.2 μg·L^{-1} (U.S. EPA 1977). At Cornwall, Ontario, municipal drinking water contained trace quantities (<1-5 μg·L^{-1}) of benzene in 1980 (Environment Canada 1984b). Intake water for industrial use from the St. Lawrence River had trace amounts (<1-5 μg·L^{-1}) of benzene in one of two samples taken in a 1980 survey (Environment Canada 1984b). Concentration ranges for benzene in raw water at treatment plant intakes in the upper Niagara River during 1979 and 1980 are presented in Table 6-87. Sampling results for benzene are not reported in NAQUADAT (1985).

6.3.6.1.4 Forms and Fate in the Aquatic Environment

Benzene (molecular formula C_6H_6, molecular weight 78.1) is a volatile, colourless liquid hydrocarbon with a water solubility of 1750 mg·L^{-1} at 10°C and a vapour pressure of 12.7 kPa at 10°C (Mackay and Leinonen 1975). Although very

Table 6-87. Concentration Ranges for Benzene in Raw Water at Treatment Plant Intakes in the Upper Niagara River in 1979 and 1980

Sample location	Year	Number of samples	Number of samples containing benzene	Concentration range ($\mu g \cdot L^{-1}$)
Niagara-on-the-Lake	1979	9	4	ND[1]-0.263
	1980	14	8	ND-0.06
Niagara Falls	1979	9	5	ND-0.059
	1980	13	9	ND-1.2
Fort Erie	1979	9	5	ND-2.2
	1980	14	10	ND-0.3
St. Catharines	1980	8	6	ND-0.6

[1] ND = not detected.

Source: Environment Canada/Ontario Ministry of the Environment 1981

little is known about its environmental fate, volatilization with subsequent atmospheric oxidation is considered to be its primary fate. Some biodegradation may take place over an extended time period (U.S. EPA 1979).

Sorption by silty sandy loam soils and montmorillonite clay was found to be minimal (Rogers *et al.* 1980). Calculated values of the octanol/water partition coefficient for benzene vary from 1.95 (Leo *et al.* 1971) to 2.13 (Chiou *et al.* 1977).

Because benzene absorbs light at wavelengths below 290 nm, direct photolysis in the water column is not expected. Likewise, hydrolysis and oxidation are not expected to be important in natural surface waters (U.S. EPA 1979).

Volatilization is expected to be significant, especially from turbulent, well-mixed, shallow waters. Volatilization half-lives of 4.81 h at 25°C and 5.03 h at 10°C were predicted for the loss of benzene from a 1-m column of water (Mackay and Leinonen 1975). Estimated atmospheric half-lives of 2.4 to 24 h have been obtained from smog chamber studies (Darnall *et al.* 1976).

Some species of bacteria have been found that are able to utilize benzene as a sole source of carbon (Zobell 1950; Claus and Walker 1964; Gibson 1976). There have been indications that benzene may be degraded during biological sewage treatment provided that suitable acclimatization can be achieved (Thom and Agg 1975). It has been suggested, however, that benzene will be resistant to biodegradation in dilute aqueous systems (Helfgott *et al.* 1977).

6.3.6.1.5 References

Chiou, C.T., V.H. Freed, D.W. Schmedding and R.L. Kohnert. 1977. Partition coefficients and bioaccumulation of selected organic chemicals. Environ. Sci. Technol. 11: 475-478.

Claus, D. and N. Walker. 1964. The decomposition of toluene by soil bacteria. J. Gen. Microbiol. 36: 107-122. (Cited in U.S. EPA 1979.)

CORPUS Information Services. 1985. Benzene. CPI Product Profiles. Don Mills, Ontario.

Darnall, K.R., A.C. Lloyd, A.M. Winer and J.N. Pitts, Jr. 1976. Reactivity scale for atmospheric hydrocarbons based on reactions with hydroxyl radical. Environ. Sci. Technol. 10: 692-696. (Cited in U.S. EPA 1979.)

Duholke, W.K. and O. Meresz. 1977. Organic Compounds of Industrial Origin in the St. Clair River. Ontario Ministry of the Environment, Toronto, Ontario. Rep. No. OTC/MS-7507. (Cited in Health and Welfare Canada 1979.)

Environment Canada. 1984a. Benzene. Environmental and Technical Information for Problem Spills (EnviroTIPS). Technical Services Branch, Environmental Protection Programs Directorate, Environmental Protection Service, Ottawa. 107 pp.

Environment Canada. 1984b. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Gibson, D.T. 1976. Initial reaction in the bacterial degradation of aromatic hydrocarbons. Zentralbl. Bakteriol. Parasitenkd. Infektionskr. Hyg. Abt. 1 Orig. Reihe B 162: 157-168. (Cited in U.S. EPA 1979.)

Health and Welfare Canada. 1979. Benzene. Health Protection Branch, Environmental Health Directorate, Ottawa. Publ. No. 79-EHD-40. 161 pp.

Helfgott, T.B., F.L. Hart and R.G. Bedard. 1977. An Index of Refractory Organics. Office of Research and Development, U.S. Environmental Protection Agency, Oklahama. EPA 600/2-77-174. 131 pp.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rogers, R.D., J.C. McFarlane and A.J. Cross. 1980. Adsorption and desorption of benzene in two soils and montmorillonite clay. Environ. Sci. Technol. 14: 457-460.

Sheffield, A. 1979. National Inventory of Sources and Emissions of Benzene (1976). Environmental Protection Service, Environment Canada, Ottawa. Rep. No. EPS 3-AP-79-4.

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

Smillie, E.S., A.A. Nicholson, O. Meresz, W.K. Duholke, G.R.V. Rees, K. Roberts and C. Fung. 1977. Organics in Drinking Waters. Ontario Ministry of the Environment, Toronto, Ontario. Rep. No. OTC-7703. (Cited in Health and Welfare Canada 1979.)

Thom, N.S. and A.R. Agg. 1975. The breakdown of synthetic organic compounds in biological processes. Proc. R. Soc. London B 189: 347-357.

U.S. EPA. 1977. The National Organic Monitoring Survey. Phases I, II and III. Office of Water Supply, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1979. Benzene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 71-1 to 71-9.

U.S. EPA. 1980. Ambient Water Quality Criteria for Benzene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-018.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Zobell, C.E. 1950. Assimilation of hydrocarbons by microorganisms. *In* Advances in Enzymology and Related Subjects of Biochemistry. Vol. 10. F.F. Nord (ed.). Interscience Publ. Inc., New York. pp. 443-486. (Cited in U.S. EPA 1979.)

6.3.6.2 Chlorinated Benzenes

6.3.6.2.1 Uses and Production

Chlorinated benzenes are used as industrial solvents, pesticides, dielectric fluids, deodorants and chemical intermediates. Monochlorobenzene is used primarily for the synthesis of *ortho-* and *para*-nitrochlorobenzenes. It is also used as a solvent and in very small amounts in the production of some pesticides. No production of monochlorobenzene occurs in Canada (Ontario Ministry of the Environment 1984).

The major uses of 1,2-dichlorobenzene are as a process solvent in certain chemical manufacturing processes and as an intermediate in the synthesis of dyestuffs, herbicides and degreasers. 1,4-Dichlorobenzene is used primarily as an air deodorant and insecticide, accounting for 90% of the total production of this isomer (Ware and West 1977). The use of 1,4-dichlorobenzene has remained essentially steady over the past 20 years in Canada. In 1979, 1500 t of 1,4-dichlorobenzene were consumed (Moore and Ramamoorthy 1985). Information is not available concerning the use of 1,3-dichlorobenzene (U.S. EPA 1980a). No production of dichlorobenzenes occurs in Canada (Ontario Ministry of the Environment 1984). 1,2,4-Trichlorobenzene is used as a dye carrier, a herbicide intermediate, a heat transfer medium, a dielectric fluid in transformers, a degreaser and a lubricant (U.S. EPA 1980b). Other trichlorobenzene isomers are not used in significant quantities. 1,2,4,5-Tetrachlorobenzene is the only tetrachloro-isomer used in industrial quantities (U.S. EPA 1980b). It is used in the production of the defoliant, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T); in the synthesis of 2,4,5-trichlorophenol; and as a fungicide. No production of trichlorobenzenes or tetrachlorobenzenes occurs in Canada (Ontario Ministry of the Environment 1984).

Pentachlorobenzene is used in small quantities as a captive intermediate in the synthesis of specialty chemicals (Ware and West 1977). Pentachlorobenzene has very limited commercial use in North America; in Europe, it is used in limited quantities to produce the pesticide pentachloronitrobenzene (Ontario Ministry of the Environment 1984). In 1972, hexachlorobenzene was used as a fungicide to control wheat bunt and smut on seed grains in the U.S.A. Other industrial uses in the U.S.A. include dye manufacturing, a porosity controller in the manufacturing of electrodes, a wood preservative and an additive in pyrotechnic compositions (U.S. EPA 1975a). Hexachlorobenzene is not produced as a product by the chemical industry, but may be produced inadvertently as a waste product of chemical manufacturing. Hexachlorobenzene is not registered in Canada at present, but its use (as a fungicide for seed and cereal treatment and as a fungicide for effective control against bunt and dwarf bunt of wheat) is listed with Agriculture Canada as acceptable for registration because there are no registered alternative chemicals (Ontario Ministry of the Environment 1984).

Importation of chlorobenzenes into Canada in 1981, 1982 and 1983 was 3840, 2657 and 2301 t, respectively (Statistics Canada 1983, 1984). Data on individual chlorobenzenes imported into Canada are presented in Table 6-88.

Table 6-88. Importation of Various Chlorobenzenes into Canada

Compound	Amount (t) 1981	1982
Monochlorobenzene	17	13
p-Dichlorobenzene (1,4-dichlorobenzene) (formula fumigants)	87	16
p-Dichlorobenzene (technical)	3637	2457
o-Dichlorobenzene (1,2-dichlorobenzene)	187	186
Trichlorobenzene	71	28
Hexachlorobenzene	7	68

Sources: Statistics Canada 1983, 1984.

6.3.6.2.2 Sources and Pathways for Entering the Aquatic Environment

Chlorinated benzenes can enter the aquatic environment as solvents, pesticides, dielectric fluids, deodorants and chemical contaminants or intermediates. They are prevalent in both solid and liquid industrial effluents and in atmospheric discharges (Ontario Ministry of the Environment 1984). It has been reported that through the chlorination of municipal sewage wastewater containing small amounts of benzene and benzene derivatives, low levels of a variety of chlorinated benzenes can be produced (Glaze and Henderson 1975; Mori *et al.* 1978).

Chlorinated benzenes can enter the aquatic environment as a result of their use; 34 278 kg of monochlorobenzene, 8182 kg of trichlorobenzene and about 1500 kg of tetra-, penta- and hexachlorinated benzene enter from this source yearly in the U.S.A. Annually, 690 kg of monochlorobenzene and 1628 kg of hexachlorobenzene contaminate solid wastes in the U.S.A. Yearly estimates of atmospheric contamination of monochlorobenzene and tetrachlorobenzenes in the U.S.A. are 362 and 909 kg, respectively (Ware and West 1977).

Hexachlorobenzene is of concern because of its widespread distribution as an environmental contaminant and a contaminant of food products used for human consumption (U.S. EPA 1980b). The St. Lawrence – Great Lakes system is a critical region for hexachlorobenzene contamination because of the numerous chlorine plants located on both sides of the border. Amounts of hexachlorobenzene entering the Great Lakes are unknown (Ontario Ministry of the Environment 1984). Levels of hexachlorobenzene in effluents sampled across Canada range from 0.02 to 1.1 $\mu g \cdot L^{-1}$ in the Atlantic region; 0.005 to 14 $\mu g \cdot L^{-1}$ in Ontario; and 0.05 to 0.11 $\mu g \cdot L^{-1}$ in the Pacific region (Environment Canada 1979).

6.3.6.2.3 Environmental Concentrations

Chlorobenzene has been detected in water monitoring surveys of various U.S. cities. The concentrations reported were as follows: 1.0 $\mu g \cdot L^{-1}$ in groundwater; 0.1-5.6 $\mu g \cdot L^{-1}$ in raw water contaminated by various discharges; 4.7 $\mu g \cdot L^{-1}$ in upland water; 8.0-17.0 $\mu g \cdot L^{-1}$ in industrial discharge; and 27 $\mu g \cdot L^{-1}$ in municipal water (U.S. EPA 1980b).

Table 6-89. Environmental Concentration Ranges for Chlorobenzenes in Canadian Surface Waters

Region	Compound	Concentration range (ng·L^{-1})	Number of samples	Sampling year(s)
Western	Hexachlorobenzene	<1[1]	1352	1980-1985
Central	Hexachlorobenzene	0.4[1]-4	296	1980-1985
Atlantic	1,3-Dichlorobenzene	<20[2]-20	92	1980-1985
	1,4-Dichlorobenzene	<20[2]-30	89	1980-1985
	1,2-Dichlorobenzene	<20[2]	90	1980-1985
	1,3,5-Trichlorobenzene	<4[3]	88	1980-1985
	1,2,4-Trichlorobenzene	<4[3]	90	1980-1985
	1,2,3-Trichlorobenzene	<4[3]	90	1980-1985
	1,2,3,5-Tetrachlorobenzene	<2[4]	88	1980-1985
	1,2,4,5-Tetrachlorobenzene	<2[4]	90	1980-1985
	1,2,3,4-Tetrachlorobenzene	<2[4]	90	1980-1985
	Pentachlorobenzene	<2[4]	90	1980-1985
	Hexachlorobenzene	<2[1]	90	1980-1985

[1] Detection limit is 1 ng·L^{-1}.
[2] Detection limit is 20 ng·L^{-1}.
[3] Detection limit is 4 ng·L^{-1}.
[4] Detection limit is 2 ng·L^{-1}.

Source: NAQUADAT 1985.

Environmental concentration ranges for chlorobenzenes in Canadian surface waters are presented in Table 6-89. Di-, tri- and hexachlorobenzenes have been found in the Niagara River and have been attributed to probable leaching from toxic waste disposal sites along the river (Oliver and Nicol 1984).

In the National Organics Reconnaissance Survey (NORS) conducted by the U.S. Environmental Protection Agency in 1975, hexachlorobenzene was found in 3 of the 10 drinking water supplies sampled, at concentrations ranging from 6 to 10 ng·L^{-1} (U.S. EPA 1975b).

6.3.6.2.4 Forms and Fate in the Aquatic Environment

The chlorination of benzene yields 12 different chlorinated isomers: chlorobenzene (monochlorobenzene), three dichlorobenzenes, three trichlorobenzenes, three tetrachlorobenzenes, pentachlorobenzene and hexachlorobenzene (Table 6-90). The environmental dynamics of individual chlorinated benzene isomers in aquatic systems will depend, in part, on their individual physical and chemical properties. Because of the various degrees of chlorination, chlorinated benzenes will undergo varying rates of movement in the aquatic environment (U.S. EPA 1979; Ontario Ministry of the Environment 1984).

Many of the properties of chlorinated benzenes may be related to the degree of chlorination and to the molecular weight of the individual isomer (Table 6-90). Melting points and boiling points tend to increase with increasing molecular weight and chlorine substitution. Vapour pressure decreases with increasing molecular weight such that the higher the degree of chlorination, the lower the volatility. Conversely, water solubility decreases with increasing molecular weight. Air/water partition coefficients (Henry's law constants), which are derived from volatility and solubility data, also decrease with increasing molecular weight. Chlorinated benzenes are essentially lipophilic in nature, and, hence, have relatively high octanol/water partition coefficients. Partitioning to lipids increases with increasing molecular weight and chlorine substitution (U.S. EPA 1979; Ontario Ministry of the Environment 1984).

Chlorinated benzenes are essentially ubiquitous in the aquatic environment; they have been detected in water, sediments and aquatic biota (Oliver and Niimi 1983; Ontario Ministry of the Environment 1984). Because they are relatively resistant to abiotic and biotic degradation, they tend to persist in the environment. The major removal processes for these compounds are considered to be sorption, volatilization and bioaccumulation (U.S. EPA 1979).

Aryl halides, which include chlorinated benzenes, are characterized by their very low reactivity towards nucleophilic reagents (Morrison and Boyd 1971). Hence, hydrolytic processes involving chlorinated benzenes are not expected in aquatic systems (U.S. EPA 1979).

Sorption may be a significant removal process for several chlorinated benzenes in the aquatic environment. Chlorinated benzenes are generally hydrophobic, having high octanol/water partition coefficients (Table 6-90). Based on available information, the chlorinated benzenes, particularly the higher-molecular-weight compounds, may concentrate on particulate matter to concentrations that are several orders of magnitude greater than those in the water column. For example, 1,2,4-trichlorobenzene was found to be readily adsorbed to acclimated microorganisms in sewage treatment plants (Simmons *et al.* 1976). Hexachlorobenzene was found in sediments near industrial activity at concentrations up to several orders of magnitude above those found in the water column (Laska *et al.* 1976; Laseter *et al.* 1976). Eleven isomers of chlorinated benzenes were examined in the raw sewage and treated effluents from four activated sludge wastewater treatment plants in Ontario. Removals of 75-95% were estimated, with volatilization and adsorption to sludge biomass being the probable removal mechanisms (Oliver and Nicol 1982). Surveys of Lake Superior, Lake Huron, Lake Erie and Lake Ontario indicated that chlorinated benzenes were concentrated in sediments. Concentration profiles in lake sediments indicated that

Table 6-90. Physical-chemical and Biological Properties of Chlorinated Benzenes

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure[1] (kPa) at 20-25°C	Water solubility[1] ($mg \cdot L^{-1}$) at 25°C	Henry's law constant[1] ($kPa \cdot m^3 \cdot mol^{-1}$)	Octanol/water partition coefficient[2] (log P_{ow})	Bioconcentration factor, log BCF (water concentration in $ng \cdot L^{-1}$)[3]
Chlorobenzene	112.56	−45.6	132	1.581	491	0.363	2.84[4]	2.81[5]
1,2-Dichlorobenzene	147.01	−17.0	180.5	0.196	134	0.195	3.40	2.43 ± 1.32 (47 ± 17)
1,3-Dichlorobenzene	147.01	−24.7	173	0.307	122	0.366	3.44	2.62 ± 1.63 (28 ± 5)
1,4-Dichlorobenzene	147.01	53.1	174	0.090	83.2	0.160	3.37	2.57 ± 1.86 (28 ± 5)
1,2,3-Trichlorobenzene	181.45	53	218	0.053	24.0	0.234	4.11	3.08 ± 2.40 (4.3 ± 2)
1,2,4-Trichlorobenzene	181.45	16.95	213.5	0.061	29.8	0.379	4.02	3.11 ± 2.51 (3.2 ± 2)
1,3,5-Trichlorobenzene	181.45	63	208	0.077	15.8	0.161	4.15	3.26 ± 2.38 (2.3 ± 0.4)
1,2,3,4-Tetrachlorobenzene	215.9	47.5	254	0.007	4.31	0.261	4.46	3.72 ± 2.70 (1.4 ± 0.3)
1,2,3,5-Tetrachlorobenzene	215.9	54.5	246	1.4×10^{-3}	3.5	0.593	—	—
1,2,4,5-Tetrachlorobenzene	215.9	140	243	5.4×10^{-4}	0.595	0.261	4.52	3.72 ± 2.81 (1.0 ± 0.5)
Pentachlorobenzene	250.3	86	277	5.5×10^{-3}	0.560	0.977	4.94	4.11 ± 3.11 (0.34 ± 0.1)
Hexachlorobenzene	284.8	230	322	3.4×10^{-4}	5.0×10^{-3}	5.0×10^{-3} (20°C)	5.50	4.08[6] (0.32 ± 0.3)

[1] Mean of values reported in Mackay and Shiu (1981).

[2] Measured values compiled in Oliver and Niimi (1983) judged to be the "best" values available.

[3] Bioconcentration factors taken from Oliver and Niimi (1983); continuous-flow system; chlorinated benzene in methanol; exposure concentrations indicated; whole-body tissue analysis for rainbow trout (*Salmo gairdneri*) held at 15°C.

[4] Measured value from Leo *et al.* (1971).

[5] Bioconcentration factor for mosquito fish (*Gambusia affinis*) in static system for 48 h (Lu and Metcalf 1975).

[6] Not equilibrated after 119 d (Oliver and Niimi 1983).

the compounds were persistent (Oliver and Nicol 1982). The persistence of hexachlorobenzene (Beck and Hansen 1974; Beall 1976; Isensee 1976) and pentachlorobenzene (Beck and Hansen 1974) has been demonstrated in various soils.

No information is available on the photolysis of chlorinated benzenes in the water column. It is expected that chlorinated benzenes, which are relatively volatile, will be released to the atmosphere where photolysis may then take place. Monochlorobenzene was found to photolyze slowly when irradiated in a simulated atmosphere. However, in the presence of nitric oxide, reaction rates increased resulting in an estimated half-life of approximately 9 h (Dilling *et al.* 1976). Some chlorinated benzenes are reactive towards hydroxyl radicals in air, with half-lives of approximately 3 d for dichlorobenzenes (Brown *et al.* 1975), 1-7 d for 1,2,4-trichlorobenzene (Simmons *et al.* 1976) and 2 d for hexachlorobenzene (Brown *et al.* 1975). The photooxidation of hexachlorobenzene has been studied in nonaqueous solvents; however, because of the experimental protocols employed, no estimations of photolytic rates in aqueous systems can be made (U.S. EPA 1979).

Volatilization is the dominant mechanism for the removal of chlorinated benzenes from the water column. Laboratory and field studies, along with theoretical calculations, have been used to demonstrate that several chlorinated benzenes may be efficiently volatilized from aqueous systems. Monochlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene, at concentrations of 300, 100, 300 and 100 $\mu g \cdot L^{-1}$, respectively, volatilized almost completely from aerated distilled water in less than 4 h. Volatilization from unaerated distilled water was slower, with essentially total loss occurring in less than 3 d for the compounds studied. Half-lives for these compounds in aerated distilled water were usually less than 0.5 h, whereas those for these compounds in quiescent water were generally less than 9 h (U.S. EPA 1979). In a 1-year study of 1,4-dichlorobenzene in Lake Zurich, Switzerland, volatilization was considered to be the major loss mechanism (Schwarzenbach *et al.* 1979). Hexachlorobenzene volatilized from an experimental pond with a half-life of approximately 1-3 d. However, because the concentration of hexachlorobenzene used (50 $\mu g \cdot L^{-1}$) was above the solubility limit, sorption and sedimentation also probably occurred. Calculated air/water partition coefficients indicate that several chlorinated benzenes will readily volatilize (Mackay and Shiu 1981). Using such calculated values, half-lives in the order of 0.5 d or less were predicted for the volatilization of selected chlorinated benzenes for a water column of 1-m depth (U.S. EPA 1979). The ecological significance, however, of these calculated volatilization rates must be carefully interpreted, because only one water depth is assumed with no turbulence or mixing, and competing processes, such as sorption, are not considered (U.S. EPA 1979).

Chlorinated benzenes are expected to accumulate in aquatic organisms. The bioaccumulation of various compounds has been studied by a number of investigators (U.S. EPA 1979; Ontario Ministry of the Environment 1984), with the result that bioconcentration and bioaccumulation factors for the same compound show considerable variation. Such variation can be attributed to the use of different test species, different exposure concentrations and durations and different experimental protocols. Hence, results are difficult to interpret in an ecological framework. For example, several experiments were not conducted at steady state, and, hence, equilibrium bioconcentration or bioaccumulation values cannot be reliably calculated. In one notable exception, the bioconcentration factors for 10 chlorinated benzenes were determined at equilibrium in a continuous-flow system using isomer concentrations approximating measured environmental levels (Table 6-88) (Oliver and Niimi 1983). Bioconcentration factors progressively increased with increasing molecular weight and chlorine content, and were in the order of 10^2-10^4, depending upon the particular compound studied (Oliver and Niimi 1983).

Although some chlorinated benzenes have been detected in carnivores in aquatic food webs, information on biomagnification is limited. Dietary sources contributed approximately

6 and 17% to the total body burden of bluegill sunfish (*Lepomis macrochirus*) when exposed to 1,2,4-trichlorobenzene (Macek *et al.* 1977) and hexachlorobenzene (Laseter *et al.* 1976), respectively. In contrast, laboratory feeding studies indicated that the uptake of hexachlorobenzene by rainbow trout (*Salmo gairdneri*) related directly to the concentration in the food and the duration of feeding. A high correlation was observed between expected levels and those measured in field studies for rainbow trout. These observations led the authors to speculate that in natural waters where hexachlorobenzene concentrations are low, uptake via diet could be substantially higher than from water (Niimi and Cho 1980).

Chlorinated benzenes may be biologically degraded; however, any biodegradation is expected to be slow, with the higher chlorinated isomers exhibiting greater resistance (Ware and West 1977). Several studies have indicated that, with the exception of monochlorobenzene, chlorinated benzenes are generally resistant to microbial degradation during sewage and industrial wastewater treatment (Gibson *et al.* 1968; Thom and Agg 1975; Simmons *et al.* 1976; Ware and West 1977). The metabolism of several chlorinated benzenes was studied in the frog (*Rana pipiens*); approximately 1% or less of the initial dose was converted to metabolites. Several metabolic products, such as chlorinated phenols and catechols, were identified in model ecosystems containing monochlorobenzene and hexachlorobenzene (Lu and Metcalf 1975).

6.3.6.2.5 References

Beall, M. 1976. Persistence of aerially applied HCB on grass and soil. J. Environ. Qual. 5: 367-369.

Beck, J. and K. Hansen. 1974. The degradation of quintozene, pentachlorobenzene, hexachlorobenzene and pentachloroaniline in soil. Pestic. Sci. 5: 41-48. (Cited in Isensee *et al.* 1976.)

Brown, S., F. Chan, J. Jones, D. Liu, K. McCaleb, T. Mill, K. Supios and D. Schendel. 1975. Research Program on Hazard Priority Ranking of Manufactured Chemicals. Phase II. Final Report. Stanford Research Institute, Menlo Park, California. (Cited in Ontario Ministry of the Environment 1984.)

Dilling, W.L., C.J. Bredweg and N.B. Tefertiller. 1976. Simulated atmospheric decomposition rates of methylene chloride, 1,1,1-trichloroethane, trichloroethylene and other compounds. Environ. Sci. Technol. 10: 351-356.

Environment Canada. 1979. Hexachlorobenzene (HCB) in Canada. Three Reports to the Department of the Environment/Department of National Health and Welfare Environmental Contaminants Committee, Environmental Protection Service, Ottawa. 59 pp.

Gibson, D., J. Koch, C. Schuld and R. Kallio. 1968. Oxidative degradation of aromatic hydrocarbons by microorganisms. II. Metabolism of halogenated aromatic hydrocarbons. Biochemistry 11: 3795-3802.

Glaze, W.H. and J.E. Henderson. 1975. Formation of organochlorine compounds from chlorination of municipal secondary effluent. J. Water Pollut. Control Fed. 47: 2511-2515.

Isensee, A.R., E.R. Holden, E.A. Woolson and G.E. Jones. 1976. Soil persistence and aquatic bioaccumulation potential of hexachlorobenzene. J. Agric. Food Chem. 24: 1210-1214.

Laseter, J.L., C.K. Bartell, A.L. Laska, D.G. Holmquist, D.B. Condie, J.W. Brown and R.L. Evans. 1976. An Ecological Study of Hexachlorobenzene. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA 560/6-76-009. 560 pp.

Laska, A.L., C.K. Bartell and J.L. Laseter. 1976. Distribution of hexachlorobenzene and hexachlorobutadiene in water, soil and selected aquatic organisms along the lower Mississippi River, Louisiana. Bull. Environ. Contam. Toxicol. 15: 535-542.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

Lu, P.-Y. and R.L. Metcalf. 1975. Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. Environ. Health Perspect. 10: 269-284.

Macek, K.J., S.R. Petrocelli and B.H. Sleight. 1977. Considerations in Assessing the Potential for, and Significance of Biomagnification of Chemical Residues in Aquatic Food Chains. *In* Proc. 2nd Annual Symp. on Aquatic Toxicology. ASTM STP 667. L.L. Marking and R.A Kimerle (eds.). American Society for Testing and Materials, Cleveland, Ohio.

Mackay, D. and W.Y. Shiu. 1981. A critical review of Henry's Law Constants for chemicals of environmental interest. J. Phys. Chem. Ref. Data 10: 1175-1199.

Moore, J.W. and S. Ramamoorthy. 1985. Organic Chemicals in Natural Waters. Applied Monitoring and Impact Assessment. Springer-Verlag Inc., New York. p. 46.

Mori, B.T., K.J. Hall and J.N. Blazevich. 1978. Effects of chlorination on some volatile organics in primary municipal sewage effluent. J. Environ. Sci. Health A13: 445-467.

Morrison, R. and R. Boyd. 1971. Organic Chemistry. 2nd edition. Alyn and Bacon, Inc., Boston, Massachusetts. 1204 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Niimi, A.J. and C.Y. Cho. 1980. Uptake of hexachlorobenzene from feed by rainbow trout (*Salmo gairdneri*). Bull. Environ. Contam. Toxicol. 24: 834-839.

Oliver, B.G. and K.D. Nicol. 1982. Chlorobenzenes in sediments, water and selected fish from Lakes Superior, Huron, Erie and Ontario. Environ. Sci. Technol. 16: 532-536.

Oliver, B.G. and K.D. Nicol. 1984. Chlorinated contaminants in the Niagara River, 1981-1983. Sci. Total Environ. 39: 57-70.

Oliver, B.G. and A.J. Niimi. 1983. Bioconcentration of chlorobenzenes from water by rainbow trout: correlations with partition coefficients and environmental residues. Environ. Sci. Technol. 17: 287-291.

Ontario Ministry of the Environment. 1984. Chlorinated Benzenes in the Aquatic Environment. Scientific Criteria Document for Standard Development. No. 3-84. Water Resources Branch, Toronto, Ontario.

Schwarzenbach, R.P., E. Molnar-Rubica, W. Giger and S.G. Wakeham. 1979. Distribution, residence time and fluxes of tetrachloroethylene and 1,4-dichlorobenzene in Lake Zurich, Switzerland. Environ. Sci. Technol. 13: 1367-1373.

Simmons, P., D. Branson and R. Bailey. 1976. 1,2,4-Trichlorobenzene: biodegradable or not? Can. Assoc. Text. Colour. Chem. Int. Tech. Conf., Quebec, Canada. (Cited in Ontario Ministry of the Environment 1984.)

Statistics Canada. 1983. Imports: Merchandise Trade and Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade and Commodity Detail 1983. Catalogue No. 65-207.

Thom, N.S. and A.R. Agg. 1975. The breakdown of synthetic organic compounds in biological processes. Proc. R. Soc. London B 189: 346-357.

U.S. EPA. 1975a. Survey of Industrial Processing Data: Task I, Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processes. Mid. Res. Inst., Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1975b. Preliminary Assessment of Suspected Carcinogens in Drinking Water. U.S. Environmental Protection Agency. Rep. Congr. No. PB-250961.

U.S. EPA. 1979. Chlorobenzene. 1,2-Dichlorobenzene. 1,3-Dichlorobenzene. 1,4-Dichlorobenzene. 1,2,4-Trichlorobenzene. Hexachlorobenzene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 72-1 to 72-19, 73-1 to 73-8, 74-1 to 74-8, 75-1 to 75-8, 76-1 to 76-10, and 77-1 to 77-13.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Dichlorobenzenes. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-039.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Chlorinated Benzenes. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-028.

Ware, S.A. and W.L. West. 1977. Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes. U.S. Environmental Protection Agency, Washington, D.C. EPA 560/2-77-004. 283 pp.

6.3.6.3 Chlorinated Phenols

6.3.6.3.1 Uses and Production

Chlorinated phenols are used as disinfectants, biocides, preservatives, dyes, pesticides and industrial and medical organic chemicals (Health and Welfare Canada 1980; U.S. EPA 1980a; Jones 1981; NRCC 1982). Pentachlorophenol is used as a wood preservative and as a bactericide and fungicide in the processing of paints, leather and fabric (Cserjesi and Johnson 1972; Larsen *et al.* 1972).

o-Chlorophenol and *p*-chorophenol are used in industry, whereas *m*-chlorophenol has limited commercial use (Jones 1981). Monochlorophenols are used as antiseptics and as intermediate feedstocks in the manufacture of higher chlorophenols and chlorocresols for biocide production. *o*-Chlorophenol is also used to form intermediates in the production of phenolic resins, and has been utilized in the extraction of sulphur and nitrogen compounds from coal (U.S. EPA 1980a).

Of the 10 isomers of dichlorophenol, only 2,4-dichlorophenol is in use as a primary chemical in Canada (Ontario Ministry of the Environment 1984). It is used as an intermediate in the manufacture of some phenoxy herbicides (Jones 1981). 2,4-Dichlorophenol is also used as a chemical intermediate in the production of germicides, temporary soil sterilants, plant growth regulators, moth-proofing agents, seed disinfectants, miticides and wood preservatives (U.S. EPA 1980b).

Of the six isomers of trichlorophenol, only 2,4,5-trichlorophenol and 2,4,6-trichlorophenol have commercial uses. 2,4,5-Trichlorophenol is used in the U.S.A. to manufacture the insecticide Ronnel, which is used extensively in Canada on livestock (Jones 1981). Both trichlorophenol isomers and tetrachlorophenols are used as wood preservatives when in combination with other compounds (notably pentachlorophenol). 2,4,5-Trichlorophenol is also used in the production of hexachlorophene, which is used in disinfectants and sanitation products for domestic, hospital and veterinary use (Ontario Ministry of the Environment 1984).

2,3,4,6-Tetrachlorophenol is the only one of three tetrachlorophenol isomers that is of commercial utility (Jones 1981). It is usually used along with pentachlorophenol as an active ingredient in wood preservatives. Commercial pentachlorophenol preparations usually contain 3-10% tetrachlorophenol, and are used in agriculture to prevent wood decay (Jones 1984).

Pentachlorophenol is the most widely used chlorophenol in industry. It is available as pentachlorophenol or as the sodium salt. Pentachlorophenol, often together with tetrachlorophenol, is an active ingredient in wood preservatives for long-term wood preservation and short-term protection (Jones 1984). In 1980, Agriculture Canada suspended many of the domestic and commercial uses of wood preservatives containing pentachlorophenol, including wood preservatives on food containers and on lumber used for seed flats, stakes and in greenhouses, and wood preservatives on above-ground interior woodwork of farm buildings (Jones 1984).

Table 6-91. Importation of Chlorophenols into Canada

Compound	Amount (t) 1981	1982	1983
Chlorinated phenols (total)	735	574	862
p-Chlorophenol	—	4	NA[1]
Trichlorophenol	1	—	NA
Pentachlorophenol	356	235	NA
p-Chlorometaxylenol	17	14	NA
Hexachlorophene	7	8	NA
Sodium pentachlorophenate[2]	15	—	—
Chlorinated phenol derivatives (group not specified)	340	313	NA

[1] NA = not available.

[2] Suspended for use, in 1980, as a fungicide in mushroom houses and on tools for mushroom culture (Jones 1984).

Source: Statistics Canada 1983.

Higher chlorinated phenols, including tri-, tetra- and pentachlorophenols, contain polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans as impurities (Jones 1981).

Suspensions of use for all chlorophenols contained in wood preservatives and wood stains for interior home use were also announced in July, 1980. Other suspensions of chlorophenols and their sodium salts included use as herbicides and soil sterilants, fungicides for mushrooms, microbiocides in curing hides and slimicides in pulp and paper operations (Jones 1984).

Until 1983, 2,4-dichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol were manufactured in Alberta, but production has since stopped. In 1982, 1800 t of pentachlorophenol were produced in Canada. Production values for 2,4-dichlorophenol and 2,3,4,6-tetrachlorophenol are unavailable (CORPUS Information Services 1983). In 1981, the following estimates were made for chlorophenols in Canada: total production, 4000 t; total imports, >2633 t; total exports, 1449 t; and total consumption, >5266 t (Jones 1984). Importation data for chlorophenols are presented in Table 6-91.

6.3.6.3.2 Sources and Pathways for Entering the Aquatic Environment

Chlorinated phenols are released into the aquatic environment via industrial effluents from pulp and paper operations and wood treatment plants and via leaching of agricultural products (Health and Welfare Canada 1980). Chlorinated phenols are also formed by chlorination of sewage treatment plant effluents and drinking water that contain phenols (U.S. EPA 1979). Total release to the environment of chlorophenols has been estimated at more than 1365 t for 1981 (Jones 1984).

Various chlorophenol compounds and isomers are produced as intermediate metabolites in the microbial breakdown of the herbicides 2,4-D and 2,4,5-T and the pesticides Silvex, Ronnel, lindane, pentachloronitrobenzene and benzene

Table 6-92. Concentrations of Three Chlorophenols at Various Distances from a Pulp and Paper Discharge Source at Jackfish Bay, Lake Superior

Chlorophenol	Concentration ($\mu g \cdot L^{-1}$) at following distance from source (km): 0.03	1.03	1.53
2,4,6-Trichlorophenol	3.3	NM[1]	0.2
2,3,5,6-Tetrachlorophenol	0.6	0.06	ND[2,3]
Pentachlorophenol	0.54	0.065	ND[3]

[1] NM = not measured.
[2] ND = not detected.
[3] Detection limit is 0.05 $\mu g \cdot L^{-1}$.

Source: Cherwinsky 1983.

hexachloride (U.S. EPA 1980a; Ontario Ministry of the Environment 1984). A study in 1979 in Wood Lake (pH 8), British Columbia, reported the detection of 2,4-dichlorophenol in the lake sediments at a depth of 0-2 cm. This chlorinated phenol was a degradation product of 2,4-D butoxyethanol ester, which had been applied to the lake to control Eurasian water milfoil. Highest concentrations ($\approx 0.7\ \mu g \cdot g^{-1}$) of 2,4-dichlorophenol occurred between 11 and 19 d after treatment (Jones 1984). Another study, in which an initial concentration of 1.5 $mg \cdot L^{-1}$ of 2,4-D was added to an outdoor pond, demonstrated the presence of 2,4-dichlorophenol in water samples up to 125 d after treatment (Scott *et al.* 1982). It has also been demonstrated that lindane is decomposed to pentachlorophenol, and that chlorophenoxyacetic acids (including 2,4-D) are degraded to 2,4,5-trichlorophenol (Health and Welfare Canada 1980).

Of 10 water samples taken from Thunder Bay near a pulp and paper mill discharge, 1 sample contained 4 $\mu g \cdot L^{-1}$ dichlorophenols and 2 contained 3 and 23 $\mu g \cdot L^{-1}$ trichlorophenols, respectively (Robinson and Smillie 1977). Concentrations of chlorophenols decreased with increasing distance from a pulp and paper wastewater discharge in Jackfish Bay, Lake Superior (Table 6-92).

Concentrations of various chlorophenols in industrial effluents and lagoons in New Brunswick and Nova Scotia are presented in Table 6-93.

Thirteen sewage effluent samples from 7 treatment plants in Ontario all contained pentachlorophenol ranging in concentration from 65 to 1300 $ng \cdot L^{-1}$ (Fox 1978).

Groundwater at a wood treatment facility at Thunder Bay had concentrations of pentachlorophenol ranging from 2.05 to 3.35 $mg \cdot L^{-1}$ (Thompson *et al.* 1978).

There is no available information on concentrations of chlorophenols in the air in Canada (Jones 1984). However, pentachlorophenol was detected in snow samples at eight sites in Ontario during the winter of 1977/1978. The concentrations ranged from less than 0.001 to 0.003 $\mu g \cdot L^{-1}$ of snowmelt. Many of these sites, such as Kettle Lake Provincial Park near Timmins and Fushimi Lake Provincial Park near Hearst, were relatively remote from pentachlorophenol sources (Strachan 1979).

6.3.6.3.3 Environmental Concentrations

Chlorinated phenols, particularly pentachlorophenol, are ubiquitous in the Canadian aquatic environment (Jones 1984). Rain collected in Burlington, Ontario, contained up to 10 $ng \cdot L^{-1}$ of pentachlorophenol (Fox 1983). Surface waters contained 0.002-5.69 $\mu g \cdot L^{-1}$ of pentachlorophenol, and 0.005-1.0 $\mu g \cdot L^{-1}$ tetrachlorophenols (total) were found in samples collected in 1978 in the Bay of Quinte, which has a wood preserving plant site at the head of the Bay. Concentrations tended to decrease with increasing distance from the source, and in the same ratio as the formulation of the commercial product containing the chlorophenols used at the

Table 6-93. Concentrations of Chlorophenols in Industrial Effluents and Lagoons in New Brunswick and Nova Scotia in 1980

			Chlorophenols[3]							
			2,4-DCP		2,4,6-TCP		2,3,4,6-TTCP		PCP	
Industrial sector	s[1]	n[2]	N	ML	N	ML	N	ML	N	ML
Oil refineries	4	5	4	100.3	2	1.09	1	0.89	2	0.51
Pulp and paper industries	5	8	4	5.59	2	147.8	2	37.2	7	5.92
Textile mill	1	1	1	1.72	0		0		0	
Wood preservation plant	1	1	0		0		1	0.11	1	0.28
Oil-powered thermal power generators	5	8	4	16.12	1	0.48	1	0.16	4	0.87
Coal washing facilities	3	3	3	3.53	0		0		2	0.79
Coal mines	2	2	1	1.40	0	0	0		1	1.03
Coking oven	1	1	1	3.44	1	3.28	0	1.0	1	1.70
Carpet manufacturer	1	1	1	5.30	1	4.65	1	1.25	1	2.88
Lead smelter	1	1	0		0		0		0	
Chemical plants	2	3	1	3.67	2	6.04	2	0.66	2	1.73
Tire manufacturer	1	1	1	90.98	1	4.32	1	0.54	1	1.13

Note: Percent recovery and MDL in $\mu g\ L^{-1}$ for the equivalent derivatized chlorinated anisoles were as follows: 2,4-DCP,70/0.10; 2,4,6-TCP,79/0.08; 2,3,4,6-TTCP,84/0.05; PCP,90/0.07.

[1] s = no. of sites.
[2] n = no. of samples.
[3] N = no. of samples with a chlorophenol level more than 2 times the minimum detection limit (MDL); ML = maximum level ($\mu g \cdot L^{-1}$) of chlorophenol detected.

Source: Macknight and LeBlanc 1981.

wood preserving plant. Concentrations were usually less than 0.1 $\mu g \cdot L^{-1}$ for tetrachlorophenols and below 0.05 $\mu g \cdot L^{-1}$ for pentachlorophenol in the Bay (Fox and Joshi 1984).

Water samples collected in 1978 in Lake Superior had average pentachlorophenol concentrations of 11 $\mu g \cdot L^{-1}$ at Thunder Bay and Marathon and 29 $\mu g \cdot L^{-1}$ at Michipicoten (Strachan 1979). The Atlantic region was the only region to report concentrations for pentachlorophenol on NAQUADAT. The concentrations were 0.008 and 0.38 $\mu g \cdot L^{-1}$ (detection limit 0.01 $\mu g \cdot L^{-1}$) in two samples taken prior to 1980 (NAQUADAT 1985).

In 1977, 85 whole bulk water samples from stream mouths, nearshore areas adjacent to stream mouths and interconnecting rivers and channels on the Canadian shores of the Great Lakes were analyzed for pentachlorophenol. Concentrations of pentachlorophenol ranging from less than 0.005 to 1.4 $\mu g \cdot L^{-1}$ (with transient highs up to 23.0 $\mu g \cdot L^{-1}$ after periods of heavy rainfall) were observed. Only eight sites produced samples with no detectable pentachlorophenol. The highest levels occurred in watersheds along the Lake Erie and Lake Ontario shorelines (Fox 1978).

6.3.6.3.4 Forms and Fate in the Aquatic Environment

The environmental behaviour of individual chlorinated phenol compounds may be related to their physical and chemical properties (see Table 6-94). In general, as the degree of chlorine substitution increases, melting points and boiling points increase. Volatility and water solubility decrease with increasing molecular weight. As chlorinated phenols are weak acids, their solubility markedly increases above the pK_a, because the corresponding phenolate ion is more soluble than the parent phenol. Sorption to sediments and bioaccumulation are also affected by the pH of the aqueous medium; at values above the pK_a, affinity for organic substrates decreases.

Chlorinated phenols have been identified in various compartments of the aquatic environment, and several integrated processes, such as photolysis, sorption, biodegradation and bioaccumulation, account for their environmental fate.

Sorption appears to play a significant role in the removal of some chlorinated phenols from the water column. In general, as the degree of chlorine substitution increases, the octanol/water partition coefficient of individual compounds increases, indicating a greater affinity for the organic content of sediments. Sorption does not appear to be significant for mono- and dichlorophenols (U.S. EPA 1979), although some studies indicate higher levels in sediment relative to the water column (Wegman and van den Broek 1983). For example, sediment enrichment factors of 20 and 440 for 2,6-dichloro- and 2,4-dichlorophenol, respectively, were found during sediment surveys of the Rhine River (Wegman and van den Broek 1983). Sorption to inorganic particulates was not significant. Because of their higher octanol/water partition coefficients relative to mono- and dichlorophenols, tri-, tetra- and pentachlorophenols are expected to be more quickly removed from the water column by sorption to organic-rich sediments. Sediment enrichment factors of 15-43 for tri-, 24-445 for tetra- and 20 for pentachlorophenol were found in the Rhine River study (Wegman and van den Broek 1983). In an aquarium study, sediment/water distribution coefficients of 225-259 for 2,4,6-trichlorophenol, based on dry organic content of sediment, were found (Virtanen and Hattula 1982). Sediment enrichment factors of 500-6500 were recorded for 2,3,4,6- and 2,3,5,6-tetrachlorophenol in the Bay of Quinte, Lake Ontario (Fox and Joshi 1984). Enrichment factors of 20->3000 (Pierce and Victor 1978; Fox and Joshi 1984) have been reported for pentachlorophenol. Increasing pH decreases sorption of pentachlorophenol in the pH range of natural surface waters (Ontario Ministry of the Environment 1984).

The photolytic breakdown of some chlorinated phenols has been observed in dilute aqueous solution. Although no rates were given, the degradation of dilute aqueous solutions of monochlorophenols (10^{-4}-10^{-5} M) during irradiation at 254, 296 and 313 nm was observed. Molecular 2-chlorophenol was converted to pyrocatechol, whereas the anionic form was reduced to cyclopentadienic acid, which then dimerized. Resorcinol was produced upon irradiation of 3-chlorophenol, whereas 4-chlorophenol yielded hydroquinone (Boule *et al.* 1982). Both 2- and 3-chlorophenol degraded in the presence of a photosensitizer; however, 4-chlorophenol did not require the presence of a photosensitizer to degrade (Yashura *et al.* 1977). The photolysis of dichlorophenols appears to be minimal; however, 2,4-dichlorophenol has been found to be a breakdown product of 2,4-D, and may be further degraded to catechol intermediates and succinic acid (see Section 6.3.12.3.1). 2,4,6-Trichlorophenol may be degraded under ultraviolet light in the laboratory (Freitag *et al.* 1982) but the importance of photolysis of trichlorophenols in the natural environment is unknown (U.S. EPA 1979). No information is available on the photolysis of tetrachlorophenols. Pentachlorophenol may be readily photodegraded under appropriate conditions. Rates of photolysis of pentachlorophenol at pH 3.3 (99% phenol) and 7.3 (99% phenolate ion) were found to be 5.2×10^{-7} and 2.7×10^{-5} s^{-1}, respectively. These rates correspond to half-lives of approximately 4 h at pH 7.3 and 100 h at pH 3.3 (Wong and Crosby 1981). Half-lives for pentachlorophenol in highly polluted Canadian surface waters at latitudes of 45°-60°N have been estimated to be less than 1 h in summer and less than 2 d in winter at pH 7, and less than 5.5 d in summer and up to 175 d in winter at pH 3.4 (NRCC 1982).

Because chlorinated phenols are moderately water-soluble, weakly acidic and have low vapour pressures, it is anticipated that volatilization does not play a significant role in removing these chemicals from the water column (U.S. EPA 1979). Volatilization may be important for pentachlorophenol in well-mixed, shallow surface waters below pH 5. However, above pH 6, half-lives as a result of volatilization are expected to be large (>130 d) (Klopffer *et al.* 1982).

Aquatic biota may bioconcentrate chlorinated phenols. Although highly variable, in part because of the specific organism studied and the experimental protocol, bioconcentration factors generally increase with increasing chlorine substitution. Mono- and dichlorophenols are characterized by relatively low octanol/water partition coefficients, low bioconcentration factors and rapid depuration rates. A bioconcentration factor of 214 was found for bluegill sunfish (*Lepomis macrochirus*) exposed to 9.2 $\mu g \cdot L^{-1}$ of 2-chlorophenol for 28 d (U.S. EPA 1980a); a biological half-life of less than 1 d was reported (Barrows *et al.* 1980). Calculated bioconcentration factors for 2-, 3-, and 4-chlorophenol were 16, 27 and 24,

Table 6-94. Physical-chemical Properties of Chlorinated Phenols

Compound	Molecular weight[1]	Melting point[1] (°C)	Boiling point (°C (kPa))	Vapour pressure[2] (kPa (°C))	Water solubility[3] (mol·L^{-1}) at pH 5.1, 25°C	Dissociation constant[4] (25°C)	pK_a[3,5,6]	Octanol/water partition coefficient log P_{ow}
Monochlorophenols								
2-Chlorophenol	128.56	9.0	174.9 (101.3)	0.13 (12.1)	2.1	3.2×10^{-9}	8.48, 8.65	2.19[7]
3-Chlorophenol	"	33	214 (101.3)	0.13 (44.2)	2.6	1.4×10^{-9}	9.08, 9.12	2.50[7]
4-Chlorophenol	"	43.2-43.7	219.75 (101.3)	0.13 (49.8)	2.1	6.6×10^{-10}	9.42, 9.37	2.44[7]
Dichlorophenols								
2,3-Dichlorophenol	163.00	57-59	206[4] (101.3)			3.6×10^{-7}	7.70	
2,4-Dichlorophenol	"	45	210 (101.3)	0.13 (53.0)	3.8×10^{-2}	2.1×10^{-8}	7.85	2.75
2,5-Dichlorophenol	"	59	211 (99)		slight[1]	4.5×10^{-7}	7.51	
2,6-Dichlorophenol	"	68-69	219-220 (99)			1.6×10^{-7}	6.79, 6.91	2.84[8]
3,4-Dichlorophenol	"	68	253.5 (102)		slight[1]	4.1×10^{-8}	8.59	
3,5-Dichlorophenol	"	68	.233 (101)			1.2×10^{-7}	8.59	
Trichlorophenols								
2,3,4-Trichlorophenol	197.45	83.5	sublimes			2.2×10^{-8}		
2,3,5-Trichlorophenol	"	62	248.5-249.5 (33)			4.3×10^{-8}		
2,3,6-Trichlorophenol	"	58	272 (101.3)[4]			7.4×10^{-8}	5.98	
2,4,5-Trichlorophenol	"	68-70.5	sublimes (37)[4]	0.13 (72)	4.8×10^{-3}	3.7×10^{-8}	7.0, 7.07	3.72[9]
2,4,6-Trichlorophenol	"	65.9	246 (101.3)	0.13 (76.5)	2.2×10^{-3}	3.8×10^{-8}	6.1, 6.62	3.38[10]
3,4,5-Trichlorophenol	"	101	271-277 (99)			1.8×10^{-8}	7.83	
Tetrachlorophenols								
2,3,4,5-Tetrachlorophenol	231.98	116-117	sublimes			1.1×10^{-7}		
2,3,4,6-Tetrachlorophenol	"	70	150 (2)	0.13 (100.0)	7.9×10^{-4}	4.2×10^{-6}		4.10[8]
2,3,5,6-Tetrachlorophenol	"	115				3.3×10^{-6}	5.3	
Pentachlorophenol	266.34	191	309-310 (101)	2.4×10^{-3} (30)	5.6×10^{-5}	1.2×10^{-5}	4.8, 5.00	5.01[10]

[1] Weast 1974.
[2] Sax 1975.
[3] Blackman *et al.* 1955.
[4] Doedens 1967.
[5] Pearce and Simpkins 1968.
[6] Farquharson *et al.* 1958.
[7] Neely *et al.* 1974.
[8] Hansch and Leo 1979.
[9] Mackay 1982.
[10] Leo *et al.* 1971.

respectively, with biological half-lives of 11-15 h (Ontario Ministry of the Environment 1984). A steady-state bioconcentration factor of 12 was found when guppies (*Poecilia reticulata* Peters) were exposed to 2,6-dichlorophenol at pH 6 and 26°C (Saarikoski and Viluksela 1982). Reported values for bioconcentration factors spanned 1 order of magnitude for 2,4,5-trichlorophenol and 2 orders of magnitude for 2,4,6-trichlorophenol, thus reflecting differences in species examined and experimental procedures (Ontario Ministry of the Environment 1984). In an aquarium study, a bioconcentration factor of 10^4 was found for 2,4,6-trichlorophenol exposure (0.5 μg·L^{-1}) to various aquatic plants, invertebrates and fish (Virtanen and Hattula 1982). Exposure for 28 d of fathead minnows (*Pimephales promelas*) to 2,4,5-trichlorophenol (4.8 and 49.3 μg·L^{-1}) in Lake Superior water (total alkalinity 40.0-43.2 mg·L^{-1} as $CaCO_3$, pH 7.36-7.62, dissolved oxygen 8.02-8.42 mg·L^{-1} and temperature 22°C) resulted in a mean steady-state bioconcentration factor of 1850 (Call *et al.* 1980). Uptake was rapid, with equilibrium being attained in 1-2 d; however, depuration was equally rapid, with a half-life of 12 h (Call *et al.* 1980). Surveys of the Bay of Quinte, Lake Ontario, revealed tetrachlorophenol concentration factors of 10^5 in leeches and 10^4 in *Cladophora* (Fox and Joshi 1984).

Pentachlorophenol concentration factors of 60 to 5000 for invertebrates, 9100-15 000 for fish and 400 for *Cladophora* were also reported (Fox and Joshi 1984). Sunfish, bass and catfish concentrated tetrachlorophenols and pentachlorophenol after a pentachlorophenol spill in a small Mississippi lake (for tetrachlorophenols, factors were 20-221 for muscle and 40-8590 for liver tissue; for pentachlorophenol, factors were 59-514 for muscle and 176-6000 for liver tissue) (Pierce and Victor 1978). A bioconcentration factor of approximately 200 for pentachlorophenol exposure to rainbow trout (*Salmo gairdneri*) was found (Niimi and McFadden 1982); the biological half-life in trout was estimated to be less than 7 d (Niimi and Cho 1982). In general, concentration factors are below 200 for mono- and dichlorophenols, but may reach 10^4 for higher chlorinated compounds. Although uptake from water is relatively rapid, depuration is also rapid, with half-lives of less than 2 d for mono- and dichlorophenols and less than 10 d for higher chlorinated phenols (Ontario Ministry of the Environment 1984).

Biodegradation appears to be the primary mechanism responsible for removal of chlorinated phenols from surface waters. The half-lives for microbial biodegradation of monochlorophenols have been estimated at 1-26 d in natural surface waters (U.S. EPA 1979). Total degradation of 2-, 3- and 4-chlorophenol (100 mg·L^{-1}) in 2-3 d by activated sludge was observed (Ingols *et al.* 1966). Activated sludge takes up to 20 d to effect almost complete removal if chlorophenols are the only source of carbon (Pitter 1976). Numerous bacteria have been identified that are capable of degrading 2,4-dichlorophenol, although relatively little information is available on degradation in natural water (U.S. EPA 1979). 2,4-Dichlorophenol ($100\ \mu g \cdot L^{-1}$) was completely eliminated in 9 d (half-life of 6 d) in buffered (pH 7.1-7.8), biologically active lake water, although volatilization was not taken into account (Aly and Faust 1964). Under low oxygen conditions, 2,4-dichlorophenol exhibited greater resistance to microbial degradation with significant levels remaining after 43 d (Aly and Faust 1964). Several studies have reported microbial degradation of trichlorophenols in bacterial cultures and during sewage treatment (Ontario Ministry of the Environment 1984). Seventy percent of a $1\ mg \cdot L^{-1}$ solution of 2,4,5- and 2,4,6-trichlorophenol was degraded in 35 d and 9-18 d, respectively, in a freshwater nutrient medium. In comparison, 75-90 d were required to degrade pentachlorophenol to the same extent (de Kreuk and Hanstveit 1981).

Surveys in the Bay of Quinte, Lake Ontario (Fox and Joshi 1984), and in a small Mississippi lake (Pierce and Victor 1978) indicated that sediment-associated tetrachlorophenols and pentachlorophenol were not microbially degraded. The degradation of pentachlorophenol in dark and illuminated aquaria containing pond water and sediment under aerobic and anaerobic conditions has been studied. Half-lives ranging from 13 to 80 d were recorded, with the fastest degradation occurring under illuminated, aerobic conditions (Boyle *et al.* 1980). Sewage-sludge bacteria may degrade pentachlorophenol with half-lives of less than 1 d for aerobic and 192 d for anaerobic conditions (Liu *et al.* 1981). However, under natural environmental conditions, pentachlorophenol may remain intact for extended periods. For example, pentachlorophenol underwent slow breakdown in natural sediments, with only a 12% loss in 30 d (Baker *et al.* 1980). Microbial degradation may be retarded at lower temperatures. At a temperature of 4°C, the half-life for pentachlorophenol in cultures of *Pseudomonas* isolated from stream water and soil was 80 d, compared with 8-10 d at a temperature of 20°C (Trevors 1982). In general, most studies relevant to aquatic systems support a half-life for pentachlorophenol of approximately 100 d, with higher temperatures and aerobic conditions favouring more rapid breakdown. Pentachlorophenol may, however, persist for extended periods of time in sediments (Ontario Ministry of the Environment 1984).

6.3.6.3.5 References

Aly, O.M. and S.D. Faust. 1964. Studies on the fate of 2,4-D and ester derivatives in natural surface waters. J. Agric. Food Chem. 12: 541-546. (Cited in Ontario Ministry of the Environment 1984.)

Baker, M.D., C.I. Mayfield and W.E. Inniss. 1980. Degradation of chlorophenols in soil, sediment and water at low temperature. Water Res. 14: 1765-1771.

Barrows, M.E., S.R. Petrocelli, K.J. Macek and J.J. Caroll. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. pp. 379-397.

Blackman, G.E., M.H. Parke and F. Garton. 1955. The physiological action of substituted phenols. I. Relationship between chemical structure and physiological activity. Arch. Biochem. Biophys. 54: 45-54. (Cited in Ontario Ministry of the Environment 1984.)

Boule, P., C. Guyon and J. Lemaire. 1982. Photochemistry and environment. IV. Photochemical behaviour of monochlorophenols in dilute solution. Chemosphere 11: 1179-1188.

Boyle, T.P., E.F. Robinson-Wilson, J.D. Petty and W. Weber. 1980. Degradation of pentachlorophenol in a simulated lentic environment. Bull. Environ. Contam. Toxicol. 24: 177-184.

Call, D.J., L.T. Brooke and P.-Y. Lu. 1980. Uptake, elimination and metabolism of three phenols by fathead minnows. Arch. Environ. Contam. Toxicol. 9: 699-714.

Cherwinsky, C. 1983. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

CORPUS Information Services. 1983. Pentachlorophenol (PCP). CPI Product Profiles. Don Mills, Ontario.

Cserjesi, A.J. and E.L. Johnson. 1972. Methylation of pentachlorophenol by *Trichoderma virgatum*. Can. J. Microbiol. 18: 45-49.

de Kreuk, J.F. and A.O. Hanstveit. 1981. Determination of the biodegradability of the organic fraction of chemical wastes. Chemosphere 10: 561-573.

Doedens, J.D. 1967. Chlorophenols. *In* Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 5. 2nd edition. E.A. Parolla, G.O. Schetty, F.L. Dankberg, J.J. Kerstein and L.L. Strauss (eds.). John Wiley & Sons, Toronto, Ontario. pp. 325-338.

Farquharson, M.E., J.C. Gage and J. Northover. 1958. The biological action of chlorophenols. Br. J. Pharmacol. 13: 20-24. (Cited in Ontario Ministry of the Environment 1984.)

Fox, M.E. 1978. Personal communication (to P.A. Jones). Canadian Centre for Inland Waters, Burlington, Ontario. (Cited in Jones 1981.)

Fox, M.E. 1983. Personal communication (to P.A. Jones). Canadian Centre for Inland Waters, Burlington, Ontario. (Cited in Jones 1984.)

Fox, M.E. and S.R. Joshi. 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. J. Great Lakes Res. 10: 190-196.

Freitag, D., H. Geyer, A. Kraus, R. Viswanathan, D. Kotzias, A. Attar, W. Klein and F. Korte. 1982. Ecotoxicological profile analysis: VII. Screening chemicals for their environmental behavior by comparative evaluation. Ecotoxicol. Environ. Saf. 6:60-81.

Hansch, C. and A. Leo. 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. John Wiley & Sons Inc., New York.

Health and Welfare Canada. 1980. Phenols. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 471-488.

Ingols, R.S., P.E. Gaffney and P.C. Stevenson. 1966. Biological activity of halophenols. J. Water Pollut. Control Fed. 38: 629-638.

Jones, P.A. 1981. Chlorophenols and Their Impurities in the Canadian Environment. Environmental Protection Service, Environment Canada, Ottawa. EPS 3-EC-81-2. 434 pp.

Jones, P.A. 1984. Chlorophenols and Their Impurities in the Canadian Environment: 1983 Supplement. Environmental Protection Service, Environment Canada, Ottawa. Economic and Technical Review Report. EPS 3-EP-84-3. 93 pp.

Klopffer, W., G. Kaufmann, G. Rippen and H.J. Poremski. 1982. A laboratory method for testing the volatility from aqueous solution: first results and comparison with theory. Ecotoxicol. Environ. Saf. 6: 545-559.

Larsen, R.V., L.E. Kirsch, S.M. Shaw, J.E. Christian and G.S. Born. 1972. Excretion and tissue distribution of uniformly labelled ^{14}C-pentachlorophenol in rats. J. Pharm. Sci. 61: 2004. (Cited in Health and Welfare Canada 1980.)

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 7: 525-616.

Liu, O., K. Thomson and W.M.J. Strachan. 1981. Biodegradation of pentachlorophenol in a simulated aquatic environment. Bull. Environ. Contam. Toxicol. 26: 85-90.

Mackay, D. 1982. Correlation of bioconcentration factors. Environ. Sci. Technol. 16: 274-278.

MacKnight, S.D. and R.J. LeBlanc. 1981. Chlorinated Phenols/Phthalate Esters in Industrial Effluents. Contract Rep. by MacLaren Plansearch Ltd. Environment Canada, Dartmouth, Nova Scotia. DSS File No. KE204-0-0096. (Cited in Jones 1984.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

Niimi, A.J. and C.Y. Cho. 1983. Laboratory and field analysis of pentachlorophenol (PCP) accumulation by salmonids. Water Res. 17: 1791-1795.

Niimi, A.J. and C.A. McFadden. 1982. Uptake of sodium pentachlorophenate (NaPCP) from water by rainbow trout (*Salmo gairdneri*) exposed to concentrations in the ng/L range. Bull. Environ. Contam. Toxicol. 28: 11-19.

NRCC. 1982. Chlorinated Phenols: Criteria for Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18578. 191 pp.

Ontario Ministry of the Environment. 1984. Chlorinated Phenols in the Aquatic Environment. Scientific Criteria Document for Standard Development. No. 2-84. Water Resources Branch, Toronto, Ontario.

Pearce, P.J. and R.J.J. Simpkins. 1968. Acid strengths of some substituted picric acids. Can. J. Chem. 46: 241-248.

Pierce, R.H., Jr. and D.M. Victor. 1978. The fate of pentachlorophenol in an aquatic ecosystem. *In* Pentachlorophenol: Chemistry, Pharmacology and Environmental Toxicology. K.R. Rao (ed.). Plenum Press, New York. pp. 41-52.

Pitter, P. 1976. Technical pentachlorophenol: origin and analysis of base-insoluble contaminants. Environ. Health Perspect. 5: 41-48.

Robinson, D. and R.D. Smillie. 1977. Identification and Quantitation of Phenols and Acids in Thunder Bay and St. Mary's River. Organic Trace Contaminants Section, Ontario Ministry of the Environment, Toronto, Ontario. OTC Report 7715. (Cited in Ontario Ministry of the Environment 1984.)

Saarikoski, J. and M. Viluksela. 1982. Relation between physicochemical properties of phenols and their toxicity and accumulation in fish. Ecotoxicol. Environ. Saf. 6: 501-512.

Sax, N.I. 1975. Dangerous Properties of Industrial Materials. 4th edition. Van Nostrand Reinhold Co. Ltd., New York.

Scott, B.F., E. Nagy, J. Hart and B.K. Afghan. 1982. New extraction/gc technique finds traces of water pollutants. Ind. Res. Dev. 24: 130-135. (Cited in Jones 1984.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Strachan, W.M.J. 1979. Personal communication (to P.A. Jones). Canadian Centre for Inland Waters, Burlington, Ontario. (Cited in Jones 1981.)

Thompson, G.E., H. Hasain, J. Parry and P.J. Gilbride. 1978. Hydrogeological control and clean-up of soil and groundwater contaminants at Northern Wood Preservers, Ltd. Presented at Ont. Ind. Waste Conf., June 18-21, Toronto, Ontario. (Cited in Ontario Ministry of the Environment 1984.)

Trevors, J.T. 1982. Effect of temperature on the degradation of pentachlorophenol. Chemosphere 11: 471-475.

U.S. EPA. 1979. 2-Chlorophenol. 2,4-Dichlorophenol. 2,4,6-Trichlorophenol. Pentachlorophenol. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 84-1 to 84-8, 85-1 to 85-8, 86-1 to 86-8, and 87-1 to 87-13.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Chlorinated Phenols. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-032.

U.S. EPA. 1980b. Ambient Water Quality Criteria for 2,4-Dichlorophenol. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 400/5-80-03.

Virtanen, M.T. and M.L. Hattula. 1982. The fate of 2,4,6-trichlorophenol in an aquatic continuous-flow system. Chemosphere 11: 641-649.

Weast, R.C. (ed.). 1974. CRC Handbook of Chemistry and Physics. 55th edition. Chemical Rubber Co. Press, Cleveland, Ohio.

Wegman, R.C.C. and H.H. van den Broek. 1983. Chlorophenols in river sediments in the Netherlands. Water Res. 17: 227-230.

Wong, A.S. and D.G. Crosby. 1981. Photodecomposition of pentachlorophenol in water. J. Agric. Food Chem. 29: 125-130.

Yashura, A., A. Otsuki and K. Juwa. 1977. Photodecomposition of odorous chlorophenols in water. Chemosphere 6: 1659-1664.

6.3.6.4 Dinitrotoluenes

6.3.6.4.1 Uses and Production

Dinitrotoluenes are used in the production of explosives, in the manufacture and formulation of urethane polymers, flexible and rigid foams and surface coatings and in the preparation of dyes and organic chemicals (U.S. EPA 1980; Verschueren 1983). In 1981 and 1982, 84 and 68 t, respectively, of dinitrotoluene (dinitrotoluol) were imported into Canada (Statistics Canada 1983).

6.3.6.4.2 Sources and Pathways for Entering the Aquatic Environment

Dinitrotoluenes may enter the aquatic environment via direct discharges to surface water or in sewage by manufacturing industries that make dyes, isocyanates, polyurethanes and munitions. 2,4-Dinitrotoluene has been identified downstream from chemical industries in the Rhine River in the Netherlands (U.S. EPA 1980). Dinitrotoluenes may also enter the aquatic environment through spills during transfer or transport; no specific information is, however, available for this potential source (U.S. EPA 1980).

2,4-Dinitrotoluene and 2,6-dinitrotoluene were detected in the final effluents of several chemical industries on the St. Clair River. 2,6-Dinitrotoluene was detected in 3 of 13 samples taken in 1979 and 1980, but the concentrations were not measured. 2,4-Dinitrotoluene was detected in three of six samples at a concentration range of 10-100 $\mu g \cdot L^{-1}$ (detection limit 1 $\mu g \cdot L^{-1}$) (Munro *et al.* 1985).

6.3.6.4.3 Environmental Concentrations

2,4-Dinitrotoluene and 2,6-dinitrotoluene have been identified in surface waters, industrial effluents and drinking water in the United States (Shackelford and Keith 1976).

2,4-Dinitrotoluene and 2,6-dinitrotoluene were detected in two of three samples and three of six samples, respectively, taken from the surface waters of the St. Clair River in 1979; the concentrations, however, were not measured (Munro *et al.* 1985). 2,4-Dinitrotoluene and 2,6-dinitrotoluene were sampled for in the St. Lawrence River at Cornwall, Ontario, in 1980; no detectable concentrations, however, were observed (Environment Canada 1984). Sampling results for dinitrotoluenes are not reported in NAQUADAT (1985).

6.3.6.4.4 Forms and Fate in the Aquatic Environment

There are six possible isomers of dinitrotoluene; however, limited environmentally relevant information is available only for 2,4- and 2,6-dinitrotoluene (Table 6-95) (U.S. EPA 1979;

Table 6-95. Physical-chemical Properties of 2,4- and 2,6-Dinitrotoluene

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility (mg·L^{-1} (°C))	Octanol/water partition coefficient (log P_{ow})
2,4-Dinitrotoluene	182.14	70	300 (decomposes)	1.7×10^{-5} (59)	270 (22)	2.01
2,6-Dinitrotoluene	182.14	64.66	285	—	—	2.05

Sources: U.S. EPA 1979; Verschueren 1983.

Verschueren 1983). Given the limited data available, photoreduction, sorption and biotransformation may occur under some conditions (U.S. EPA 1979).

No specific information is available on sorption to solid phases. Because 2,4- and 2,6-dinitrotoluene have relatively low calculated octanol/water partition coefficients (Table 6-95), limited sorption to organic-rich sediments may occur.

The direct photolysis of dinitrotoluenes in the water column is not anticipated, although photoreduction of the nitro group to hydroxylamino-, nitroso- or amino- groups, together with oxidation of the methyl group to alcohol, aldehyde or carboxylic acid groups, is possible. No environmental data, however, are available (U.S. EPA 1979).

Neither oxidation nor direct hydrolysis of dinitrotoluenes is considered important in the aquatic environment. Because of its low vapour pressure and moderate water solubility, 2,4-dinitrotoluene is not expected to volatilize appreciably from the water column. Half-lives of hundreds of days have been estimated for 2,4- and 2,6-dinitrotoluene (Moore and Ramamoorthy 1984). Although no information is available, other dinitrotoluenes are probably similarly nonvolatile (Mackay and Leinonen 1975; U.S. EPA 1979).

Dinitrotoluenes were found to be resistant to biodegradation by soil microorganisms (Alexander and Lustigman 1966). Biodegradation by *Azotobacter agilis* was slow (Bringmann and Kuehn 1972). Dinitrotoluenes were found to be persistent in reservoirs (Galuzova 1963). The nitro group of 2,4-dinitrotoluene was reduced by the fungus *Mucrosporium* (McCormick *et al.* 1978).

Given their limited affinity for hydrophobic materials, bioaccumulation of dinitrotoluenes in the aquatic environment is not expected to be significant (U.S. EPA 1979). No bioaccumulation data for dinitrotoluenes in aquatic organisms are available (U.S. EPA 1980).

6.3.6.4.5 References

Alexander, M. and B.K. Lustigman. 1966. Effect of chemical structure on microbial degradation of substituted benzenes. J. Agric. Food Chem. 14: 410-413. (Cited in U.S. EPA 1979.)

Bringmann, G. and R. Kuehn. 1972. Biological decomposition of nitrotoluenes and nitrobenzenes by *Azotobacter agilis*. Gesund. Ing. 92: 273-276. (Cited in U.S. EPA 1979.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Galuzova, L.V. 1963. Maximum permissible concentration of dinitrotoluene in the water of reservoirs. Gig. Sanit. 28: 14-19. (Cited in U.S. EPA 1979.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

McCormick, N.G., J.H. Cornell and A.M. Kaplan. 1978. Identification of biotransformation products from 2,4-dinitrotoluene. Appl. Environ. Microbiol. 35: 945-948.

Moore, J.W. and S. Ramamoorthy. 1984. Organic Chemicals in Natural Waters. Applied Monitoring and Impact Assessment. Springer-Verlag, New York. 289 pp.

Munro, J.R., M.A. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-80. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Shackelford, W.M. and L.H. Keith. 1976. Frequency of Organic Compounds Identified in Water. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/4-76-062. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1979. 2,4-Dinitrotoluene. 2,6-Dinitrotoluene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 81-1 to 81-8 and 82-1 to 82-8.

U.S. EPA. 1980. Ambient Water Quality Criteria for Dinitrotoluene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-045.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.6.5 Ethylbenzene

6.3.6.5.1 Uses and Production

Ethylbenzene (phenylethane) is used in the manufacture of styrene and acetophenone. It is also used as a solvent and an asphalt and naphtha constituent (Verschueren 1983). Its major uses in Canada are in the manufacture of styrene and as a solvent in the chemical, paint and rubber industries (Environment Canada 1984a).

Current Canadian production of ethylbenzene occurs in the Sarnia area in Ontario and, since 1984, at Scotford, Alberta. Total Canadian production in 1983 and 1984 was estimated at 390×10^3 and 440×10^3 t, respectively (CORPUS Information Services 1984). Importation data for 1983 and 1984 are not available; however, 40 and 80 t of ethylbenzene were imported into Canada in 1981 and 1982, respectively (Statistics Canada 1983). Total domestic consumption was 358.5×10^3 and 440×10^3 t in 1983 and 1984, respectively. Exportation amounted to 31.5×10^3 and 30×10^3 t for 1983 and 1984, respectively.

6.3.6.5.2 Sources and Pathways for Entering the Aquatic Environment

Ethylbenzene may be released to the environment via emissions to the atmosphere and discharge to the aquatic environment during production and use (U.S. EPA 1980). Although few quantitative data are available, a reported accidental spill of ethylbenzene via a storm sewer reached a water course, causing a fish kill; a continuous water-monitoring station approximately 600 m downstream from the spill indicated ethylbenzene was present in the water (Environment Canada 1984a).

Ethylbenzene was detected in the final effluents discharging into the Niagara River at a concentration range of 1-100 $\mu g \cdot L^{-1}$ for eight samples taken in 1979 and 1980. Only 5 of 39 samples from treated waters of treatment plants along the Niagara River had ethylbenzene concentrations ranging from 0.062 to 0.1 $\mu g \cdot L^{-1}$ (detection limit 0.2 $\mu g \cdot L^{-1}$). It has been estimated that in 1981 the total Ontario municipal and industrial trace contaminant loading to the Niagara River and its tributaries was less than 0.117 $kg \cdot d^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981). Total effluent analysis for ethylbenzene from two Canadian organic chemical plants showed concentrations of 10 and 34 $\mu g \cdot L^{-1}$ (detection limit 0.2 $\mu g \cdot L^{-1}$) (Sigma Resource Consultants Ltd. 1985).

Ethylbenzene was detected in 9 of 38 samples taken in 1980 from final effluents discharging into the St. Lawrence River at Cornwall, Ontario, at a concentration range of trace (<1-5 $\mu g \cdot L^{-1}$) to 10.9 $\mu g \cdot L^{-1}$. Cornwall municipal drinking water had trace (<1-5 $\mu g \cdot L^{-1}$) amounts of ethylbenzene in one sample taken in 1980. Total ethylbenzene loadings from 14 industrial and municipal outfalls to the St. Lawrence River at Cornwall, Ontario, were estimated at 1.45 $kg \cdot d^{-1}$ in 1980 (Environment Canada 1984b).

6.3.6.5.3 Environmental Concentrations

Concentrations of ethylbenzene in the atmosphere in the vicinity of manufacturing and refinery facilities in the United States were in the low microgram per cubic metre range (NAS 1980). Ethylbenzene has been detected ($\simeq$15 $\mu g \cdot L^{-1}$) in well water in the United States (Burnham *et al.* 1971) and in finished drinking water, effluents and ambient surface waters (Shackelford and Keith 1975).

Ethylbenzene was reported at a concentration range of 1-1000 $\mu g \cdot L^{-1}$ in the St. Clair River in nine samples taken in 1979 (detection limit 0.2 $\mu g \cdot L^{-1}$) (Munro *et al.* 1985).

Only 2 of 76 samples from the upper Niagara River had detectable ethylbenzene concentrations of less than 0.001 and 0.2 $\mu g \cdot L^{-1}$ (Gibson *et al.* 1973). Ethylbenzene was sampled for in the St. Lawrence River at Cornwall, Ontario, in 1980, but no detectable concentrations were observed (Environment Canada 1984b). Sampling results for ethylbenzene are not reported in NAQUADAT (1985).

6.3.6.5.4 Forms and Fate in the Aquatic Environment

Ethylbenzene (molecular formula C_8H_{10}, molecular weight 106.16) is a colourless liquid with a water solubility of 161.2 ± 0.9 $mg \cdot L^{-1}$ at 20°C (Sutton and Calder 1975) and a vapour pressure of 1 kPa at 20°C (Verschueren 1983). Little is known about the environmental fate of ethylbenzene, but, like other alkylbenzenes, volatilization (followed by atmospheric oxidation) is probably its primary fate (U.S. EPA 1979).

Sorption to organic material may occur to some extent (calculated log octanol/water partition coefficient of 3.15) (Tute 1971); however, no environmentally relevant studies are available (U.S. EPA 1979).

Oxidation, hydrolysis and direct photolysis of ethylbenzene in the water column are not expected (U.S. EPA 1979). Volatilization will, however, be significant. A half-life of 5-6 h for volatilization from water of 1-m depth has been estimated (Mackay and Leinonen 1975). A half-life for atmospheric oxidation of 15 h has been calculated, based on smog chamber studies (Altshuller *et al.* 1962; Laity *et al.* 1973).

Some species of bacteria have been found that are capable of utilizing ethylbenzene as a sole source of carbon (Claus and Walker 1964; Gibson *et al.* 1973). Ethylbenzene (500 $mg \cdot L^{-1}$) was partially degraded (27% of theoretical oxidation) by phenol-acclimated sludge after 12 h of oxidation (Elkins *et al.* 1956). Although no information was found on bioaccumulation in natural systems, some accumulation of ethylbenzene may be anticipated, based on its partitioning to lipophilic materials (Tute 1971).

6.3.6.5.5 References

Altshuller, A.P., I.R. Cohen, S.F. Sleva and S.L. Kopczynski. 1962. Air pollution: photooxidation of aromatic hydrocarbons. Science 138: 442-443.

Burnham, A.K., G.V. Calder, J.J. Fritz, G.A. Junk, H.J. Svec and R. Willis. 1971. Identification and estimation of neutral organic contaminants in potable water. Anal. Chem. 44: 139-142.

Claus, D. and N. Walker. 1964. The decomposition of toluene by soil bacteria. J. Gen. Microbiol. 36: 107-122. (Cited in U.S. EPA 1979.)

CORPUS Information Services. 1984. Ethylbenzene. CPI Product Profiles. Don Mills, Ontario.

Elkins, H.F., E.F. Mohler, Jr. and L.R. Kumnick. 1956. Biological oxidation of oil refinery wastes in cooling tower systems. Sewage Ind. Wastes 28: 1475-1483. (Cited in Verschueren 1983.)

Environment Canada. 1984a. Ethylbenzene. Environmental and Technical Information for Problem Spills (EnviroTIPS). Technical Service Branch, Environmental Protection Programs Branch, Environmental Protection Service. Ottawa. 93 pp.

Environment Canada. 1984b. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board. Ottawa.

Gibson, D.T., B. Gschwendt, W.K. Yeh and V.M. Kobal. 1973. Initial reactions in the oxidation of ethylbenzene by *Pseudomonas putida*. Biochemistry 12: 1520-1528.

Laity, J.L., I.G. Burstain and B.R. Appel. 1973. Photochemical smog and the atmospheric reactions of solvents. *In* Solvents: Theory and Practice. R.W. Tess (ed.). Adv. Chem. Ser. No. 124. pp. 95-112. (Cited in U.S. EPA 1979.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1980. The Alkyl Benzenes. Committee on Alkyl Benzene Derivatives, U.S. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Shackelford, W.M. and L.H. Keith. 1975. Frequency of Organic Compounds Identified in Water. U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/4-76-062. 617 pp.

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Sutton, C. and J.A. Calder. 1975. Solubility of alkylbenzenes in distilled water and seawater at 25°C. J. Chem. Eng. Data 25: 320-322.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 5: 1-77.

U.S. EPA. 1979. Ethylbenzene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 78-1 to 78-5.

U.S. EPA. 1980. Ambient Water Quality Criteria for Ethylbenzene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-048.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.6.6 Monohydric and Dihydric Phenols

6.3.6.6.1 Uses and Production

Phenols and phenolic substances are aromatic hydroxy compounds that are classified as monohydric (e.g. phenol, cresols, xylenols), dihydric (e.g. catechols, resorcinols) or polyhydric depending on the number of hydroxyl groups attached to the aromatic benzene ring (McNeely *et al.* 1979). Phenolic wastes can consist of mono-, di- and polyhydric phenols, together with aldehydes, ketones, alcohols, organic acids, gases, such as ammonia and carbon dioxide, and often cyanide, all in varying proportions (Alabaster and Lloyd 1982).

Phenolic compounds are used as general disinfectants, biocides, preservatives, dyes, pesticides and medical and industrial organic chemicals. In the plastics industry, phenol is used to manufacture phenol-formaldehyde resins. Phenol is also used in various consumer products, such as household disinfectants and medical preparations (CORPUS Information Services 1984).

Only one company, located in Quebec, produces phenol in Canada. Data on production, importation and consumption of phenol and nonylphenol (which is currently produced in Ontario) and importation data for other phenolic compounds are presented in Table 6-96. These two compounds are not exported because production just satisfies the domestic market. In Canada, during 1984, approximately 57 000 t of phenolic resins were used for manufacturing plastics, chemicals and pharmaceuticals (CORPUS Information Services 1984).

Table 6-96. Production, Consumption and Importation of Phenol and Nonylphenol and Importation of Other Phenolics in Canada

		Amount (t)		
Compound	Year	Production	Consumption	Importation
Phenol	1983	34 000	57 000	22 600
	1984	25 500	59 500	34 000
o-Cresol	1981			349
	1982			17
m-Cresol	1981			6
	1982			7
p-Cresol	1981			212
	1982			38
Xylenol and isomers	1981			62
	1982			2
Pyrocatechol	1982			1
Butylcatechol	1981			225
	1982			56
Hydroquinone (quinol)	1981			120
	1982			63
Resorcinol	1981			565
	1982			346
Phenolic resins	1982			6 670
	1983			8 160

Sources: Statistics Canada 1983; CORPUS Information Services 1984.

6.3.6.6.2 Sources and Pathways for Entering the Aquatic Environment

Phenolic compounds may occur naturally in aquatic environments, because many phenols are decomposition products of aquatic plants and decaying vegetation. The major anthropogenic point sources of phenols in aquatic systems are industrial effluents and domestic sewage. Phenolic compounds may be released by distillation of coal and wood, oil refining, chemical plants, pulp and paper mills, livestock dips, animal and human wastes and the hydrolysis, chemical oxidation and microbial degradation of phenolic pesticides (McNeely *et al.* 1979).

Phenol was found in two of eight samples taken from final effluents of various industrial and municipal plants discharging into the St. Lawrence River at Cornwall, Ontario; the concentrations, however, were not measured (Environment Canada 1984). Gross loading of phenol in 14 outfalls at Cornwall was estimated at more than 24.2 $kg{\cdot}d^{-1}$. In a survey of petrochemical plant final effluents in 1979 and 1980, phenol was detected in three samples at concentrations ranging from 1 to 10 $\mu g{\cdot}L^{-1}$ (Munro *et al.* 1985). Total Ontario municipal and industrial loadings for phenols to the Niagara River and its tributaries were estimated at less than 1.343 $kg{\cdot}d^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.6.6.3 Environmental Concentrations

Most natural sources release only trace amounts of phenolic substances to water. Phenol concentrations in Canadian surface waters are generally below 2 $\mu g{\cdot}L^{-1}$. Higher concentrations occur in areas where industries discharge their effluents. For example, in 1976, concentrations as high as 0.1 $mg{\cdot}L^{-1}$ were recorded near the discharge outfall of Algoma Steel in the St. Mary's River. Data collected in 1974, from locations downstream of major pulp and paper industries in northern Ontario,

Table 6-97. Environmental Concentration Ranges for Phenolic Material in Canadian Surface Waters

Region	Concentration range (µg·L⁻¹)	Number of samples	Sampling year(s)
Pacific	ND[1]-83	46	Prior to 1980
	ND[2]-28	417	Prior to 1980
Western	2[3]-250	1364	Prior to 1980
	1[2]-38	1761	1980-1985
Central	ND[2]-94	160	1980-1985
	ND-10 000	2227	Prior to 1980
Atlantic	5[3]-70	80	1980-1985

[1] ND = not detected.

[2] Detection limit is 0.5 $\mu g \cdot L^{-1}$ (phenolic material measured colorimetrically with 4-aminoantipyrine).

[3] Detection limit is 1 $\mu g \cdot L^{-1}$ (phenolic material measured colorimetrically with 4-aminoantipyrine).

Source: NAQUADAT 1985.

showed phenol concentrations as high as 1.05 $mg \cdot L^{-1}$ (Health and Welfare Canada 1980). Phenol was detected in five samples taken from the St. Clair River at concentrations ranging from 0.001 to 10 $mg \cdot L^{-1}$ (Munro *et al.* 1985). Phenol was detected (0.001 $mg \cdot L^{-1}$) in 9% of samples taken from the upper Niagara River in 1979, but actual concentrations were not measured (Environment Canada/Ontario Ministry of the Environment 1981). Environmental concentration ranges for phenolic material in Canadian surface waters are presented in Table 6-97.

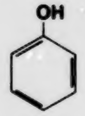
Water samples taken in 1983 and 1984 from three groundwater wells and in 1984 from two piezometer wells in Prince Edward Island were analyzed for phenolic material. A concentration below 0.01 $mg \cdot L^{-1}$ was reported for eight samples from the groundwater wells and for the two samples from the piezometer wells (NAQUADAT 1985).

6.3.6.6.4 Forms and Fate in the Aquatic Environment

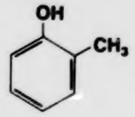
Monohydric phenols (Figure 6-4), such as phenol, *o*-, *m*- and *p*-cresol and xylenols (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-xylenol), all have relatively low vapour pressures and high water solubilities (see Table 6-98) (U.S. EPA 1979; Verschueren 1983; Windholtz *et al.* 1983). Most of the information concerning the aquatic environmental dynamics of phenols refers to the compound phenol; little or no information is available for the other monohydric phenols (Alabaster and Lloyd 1982; Verschueren 1983; Windholtz *et al.* 1983). Dihydric phenols (Figure 6-5), such as derivatives of catechol, resorcinol and quinol (hydroquinone), are known to be water-soluble and have low vapour pressures (see Table 6-98) (Verschueren 1983; Windholtz *et al.* 1983).

Photooxidation, oxidation and microbial degradation are probably the major fates of phenols in the aquatic environment. The dominance of any one of these removal mechanisms is determined by the particular conditions prevailing in each specific aqueous system (U.S. EPA 1979).

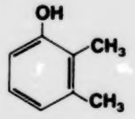
Phenol is often taken as the model compound for monohydric phenols, and, hence, most of the environmentally relevant information is available for this compound (U.S. EPA 1976). Phenol exists primarily in the un-ionized form in surface waters ($pK_a = 10.02$) (Herington and Kynaston 1957). However, coordination with dissolved or suspended di- and trivalent metal cations can markedly increase ionization, leading to enhanced solubility (U.S. EPA 1979).



Phenol



o-Cresol
(2-methylphenol)



2,3-Xylenol
(2,3-dimethylphenol)

Figure 6-4. Monohydric phenols.

Sorption appears to play a relatively minor role in the removal of phenol from the water column. Phenol, like other monohydric phenols, has a low octanol/water partition coefficient, and, hence, is not expected to sorb to organic-rich sediments. Phenol is reported to readily desorb from clay surfaces (Saltzman and Yariv 1975), and is ineffective as a flocculant for clays and soils (Chang and Anderson 1968).

In the presence of coordination or charge-transfer complexes, phenol may photolyze with the possible production of hydroquinone (quinol) (Perelshtein and Kaplan 1968; Kinney and Ivanuski 1969). *o*-Cresol may be degraded by visible light in the presence of a photosensitizer (Moussavi 1979). In addition, quinol may be photolyzed by ultraviolet light (Visser *et al.* 1977). The autoxidation of several mono- and dihydric phenols was studied in mild alkaline media at pH 7-9 and 25°C (Moussavi 1979). The oxidative half-life of phenol decreased from 26 d at pH 7 to 12 d at pH 9. *o*-Cresol was very resistant, with a half-life of 462 d at pH 9. Catechol had an oxidation half-life of 17-19 d over the pH range of pH 7-9, whereas quinol had oxidative half-lives of less than 1 h at pH 9 but 5 d at pH 7. Resorcinol had a half-life for autoxidation of 67 d at pH 9 (Moussavi 1979).

Because these compounds are relatively water-soluble and have low vapour pressures, volatilization is not expected to be a significant removal process. If any phenol is volatilized it would probably be rapidly photooxidized in the atmosphere (U.S. EPA 1979).

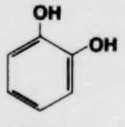
The major biotic process for the removal of phenol from the water column appears to be microbial degradation. Several laboratory studies have demonstrated the utilization of phenol as the sole carbon source for a number of isolated and

Table 6-98. Physical-chemical Properties of Some Mono- and Dihydric Phenols

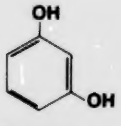
Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility (mg·L^{-1} (°C))	Octanol/water partition coefficient (log P_{ow})
Monohydric phenols						
Phenol	94.11	41	182.0	2.7×10^{-2} (20)	8.2×10^4	1.46
o-Cresol	108.13	31	191	3.2×10^{-2} (25)	3.1×10^4 (40)	
m-Cresol	"	12	202	5.3×10^{-3} (20)	2.4×10^4 (20)	
p-Cresol	"	34.8	202	5.3×10^{-3} (20)	2.4×10^4 (40)	1.92-1.94
2,3-Xylenol	122.17	73-75	217			
2,4-Xylenol	"	26	211.5	8.3×10^{-3} (20)[1]	1.7×10^5 (160)[1]	2.50[1]
2,5-Xylenol	"	71-73	212			
2,6-Xylenol	"	44-46	203			2.36
3,4-Xylenol	"	65	225			
3,5-Xylenol	"	68	219			2.35
Dihydric phenols						
Catechol	110.11	105	240 (decomposes)		4.5×10^5 (20)	0.88-1.01
Resorcinol	"	276-280		6.7×10^{-1} (138)	8.4×10^5 (0)	0.77-0.80
Quinol (hydroquinone)	"	172	218.2	5.3×10^{-1} (150)	5.9×10^5 (15)	0.50-0.59

[1] U.S. EPA 1979.

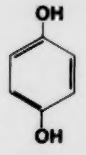
Sources: Verschueren 1983; Windholtz *et al.* 1983.



Catechol
(1,2-dihydroxybenzene)



Resorcinol
(1,3-dihydroxybenzene)



Quinol
(hydroquinone)

Figure 6-5. Dihydric phenols.

adapted microorganisms (U.S. EPA 1979). In addition, phenol degradation in natural waters has been documented. For example, phenol at an initial concentration of 0.1 mg·L^{-1} was removed at a rate of 0.03 mg·L^{-1}·h^{-1} in an *in vitro* investigation of the degrading capacity of bacteria in river water. In comparison, less than 1 μg·L^{-1}·h^{-1} of phenol was removed by sterilized samples (Visser *et al.* 1977). Aquatic organisms other than bacteria are capable of degrading phenol. For example, goldfish (*Carassius auratus*) converted phenol to phenol sulphate and rapidly eliminated it via biliary excretion (Kobayashi *et al.* 1976). Other mono- and dihydric phenols are readily degraded by activated sludge (Bunch and Chamber 1967; Bridié 1969) and by soil microflora (Alexander and Lustigman 1966), with half-lives of <1-8 d. Because these phenols have low octanol/water partition coefficients (see Table 6-98), bioaccumulation is not expected to be significant (Verschueren 1983; Windholtz *et al.* 1983). Phenols also appear to be rapidly eliminated. For example, a half-life of approximately 1 d was found for dimethylphenol as a result of depuration by bluegills (*Lepomis macrochirus*) (Barrows *et al.* 1980). *p*-Hexyl- and *p*-nonylphenols were eliminated from Atlantic salmon (*Salmo salar*) with half-lives of approximately 1 d (McLeese *et al.* 1981). A half-life of less than 4 d was found for *p*-sec-butylphenol as a result of its elimination from Atlantic salmon (McLeese *et al.* 1981).

6.3.6.6.5 References

Alabaster, J.S. and R. Lloyd. 1982. Water Quality Criteria for Freshwater Fish. 2nd edition. Butterworth Scientific, London. 361 pp.

Alexander, M. and B.K. Lustigman. 1966. Effect of chemical structure on microbial degradation of substituted benzenes. J. Agric. Food Chem. 14: 410-413.

Barrows, M.E., S.R. Petrocelli, K.J. Macek and J.J. Caroll. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. pp. 379-392.

Bridié, A.L.A.M. 1969. Determination of biochemical oxygen demand with continuous recording of oxygen uptake. Water Res. 3: 157-165.

Bunch, R.L. and C.W. Chamber. 1967. A biodegradability test for organic compounds. J. Water Pollut. Control Fed. 39: 181-187.

Chang, C.W. and J.U. Anderson. 1968. Flocculation of clays and soils by organic compounds. Soil Sci. Soc. Am. Proc. 32: 23-27.

CORPUS Information Services. 1984. Phenol (carbolic acid). Phenolic resins. CPI Product Profiles. Don Mills, Ontario.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Health and Welfare Canada. 1980. Phenols. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 471-488.

Herington, E.F.G. and W. Kynaston. 1957. The ultraviolet absorption spectra and dissociation constants of certain phenols in aqueous solution. Trans. Faraday Soc. 53: 138-142. (Cited in U.S. EPA 1979.)

Kinney, L.C. and V.R. Ivanuski. 1969. Photolysis Mechanisms for Pollution Abatement. Prepared in cooperation with Robert A. Taft Water Research Center, Cincinnati, Ohio. U.S. Environmental Protection Agency. Rep. No. TWRC-AWTRL-13. 41 pp. (Cited in U.S. EPA 1979.)

Kobayashi, K., H. Akitake and S. Kimura. 1976. Studies on the metabolism of chlorophenols in fish. VI. Turnover of absorbed phenol in goldfish. Bull. Jpn. Soc. Sci. Fish. 42: 45-50. (Cited in U.S. EPA 1979.)

McLeese, D.W., V. Zitko, D.B. Sergeant, L. Burridge and C.D. Metcalfe. 1981. Lethality and accumulation of alkylphenols in aquatic fauna. Chemosphere 10: 723-730.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Phenolic compounds. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 45-46.

Moussavi, M. 1979. Effect of polar substituents on autoxidation of phenols. Water Res. 13: 1125-1128.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Perelshtein, E.I. and V.T. Kaplan. 1968. Mechanism of the self-purification of inland surface water by the removal of phenol compounds. II. Effect of natural UV rays on aqueous solutions of phenol compounds. Gidrokhim. Mater. 48: 139-144. (Cited in U.S. EPA 1979.)

Saltzman, S. and S. Yariv. 1975. Infrared study of the sorption of phenol and *p*-nitrophenol by montmorillonite. Soil Sci. Soc. Am. Proc. 39: 474-479.

Statistics Canada. 1983. Import: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 183-185.

U.S. EPA. 1979. Phenol. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 83-1 to 83-11.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Visser, S.A., G. Lamontagne, V. Zoulalian and A. Tessier. 1977. Bacteria active in the degradation of phenols in polluted waters of the St. Lawrence River. Arch. Environ. Contam. Toxicol. 6: 455-469.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

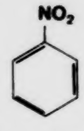


Figure 6-6. **Nitrobenzene.**

6.3.6.7 Nitrobenzenes

6.3.6.7.1 Uses and Production

Nitrobenzene is used in the production of aniline and dyestuffs. It is also used in the manufacture of rubber and photographic chemicals. Nitrobenzene is used for refining lubricants and oils, as a solvent for explosives and cellulose acetate manufacture and as a constituent of metal and shoe polish formulations (U.S. EPA 1980; Verschueren 1983). Di- and trinitrobenzenes are used in explosives (U.S. EPA 1980).

Based on 1976 estimates, the annual production of nitrobenzene in the United States ranges from 90 × 10^3 to more than 300 x 10^3 t (U.S. EPA 1980). Information on production of nitrobenzenes in Canada is unavailable. In both 1981 and 1982, 1 t of nitrobenzene was imported into Canada (Statistics Canada 1983).

6.3.6.7.2 Sources and Pathways for Entering the Aquatic Environment

During production, nitrobenzene may be lost in the effluent wash while undergoing purification (U.S. EPA 1980). Limited quantitative data are available for the entry of nitrobenzene(s) into the aquatic environment. In a 1980-1981 survey of various contaminants in industrial effluents in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of nitrobenzene were observed in 13 samples (Environment Canada 1984). In a 1979-1980 survey of effluents from petrochemical plants on the St. Clair River, nitrobenzene was detected in three of six samples; the concentrations, however, were not measured (Munro *et al.* 1985).

6.3.6.7.3 Environmental Concentrations

Nitrobenzene has been found in surface water and untreated drinking water in the United States (Shackelford and Keith 1976) and in the River Maas in the Netherlands (average concentration range, nondetectable to 0.07 $\mu g \cdot L^{-1}$) (RIWA 1974). Sampling results for nitrobenzenes are not reported in NAQUADAT (1985). Nitrobenzene was detected (detection limit 1 $\mu g \cdot L^{-1}$), but not quantified, in one of four samples taken from the St. Clair River in 1979 (Munro *et al.* 1985).

6.3.6.7.4 Forms and Fate in the Aquatic Environment

Nitrobenzenes (Figure 6-6), including mono- and dinitrocompounds, are characterized by high water solubilities, low vapour pressures and low octanol/water partition coefficients (Table 6-99) (Vershueren 1983). Very little information is available on the fate of nitrobenzenes in the aquatic environment (U.S. EPA 1979).

Table 6-99. Physical-chemical Properties of Some Nitrobenzenes

Compound	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapour pressure (kPa (°C))	Water solubility (mg·L^{-1} (°C))	Octanol/water partition coefficient (log P_{ow})
Nitrobenzene	123.1	6	211	2.0×10^{-2} (20)	1.9×10^3 (20)	1.85-1.88
1,2-Dinitrobenzene	168.1	118	319		3.8×10^3 (100)	1.58
1,4-Dinitrobenzene	168.1	173	299		1.8×10^3 (100)	1.46-1.49

Source: Verschueren 1983.

Because nitrobenzenes have relatively low octanol/water partition coefficients, sorption to organic matter is probably not significant. Sorption to inorganic matter is also likely to be minor. Although no environmentally relevant information is available for hydrolysis or oxidation, these processes are not expected to be significant (U.S. EPA 1979).

In nonaqueous solvents, nitrobenzene may be photoreduced in the presence of suitable hydrogen donors. Aniline, 4-aminophenol, azoxybenzene and benzoic acid were produced upon photolysis of a mixture of nitrobenzene and toluene (Morrison 1979). However, the significance of this process in the aquatic environment is unknown (U.S. EPA 1979).

Using reported values for water solubility and vapour pressure, the half-life of nitrobenzene as a result of volatilization from a water column of 1-m depth was predicted at approximately 185 h (Mackay and Leinonen 1975). In an aquatic model ecosystem study, only 2.2% of the nitrobenzene was recovered from the vapour-phase component (Lu and Metcalf 1975).

The decomposition of nitrobenzene by soil microflora required at least 64 d (Alexander and Lustigman 1966). Nitrobenzene, as a sole source of carbon, was readily degraded by adapted activated sewage sludge; however, 1,3- and 1,4-dinitrobenzenes were resistant to degradation (Pitter 1976). In a model ecosystem study, nitrobenzene was not degraded, nor was it accumulated or magnified in the aquatic food web (Lu and Metcalf 1975). Because of their relatively low octanol/water partition coefficients, nitrobenzenes are not expected to bioaccumulate to an appreciable extent (U.S. EPA 1979).

6.3.6.7.5 References

Alexander, M. and B.K. Lustigman. 1966. Effect of chemical structure on microbial degradation of substituted benzenes. J. Agric. Food Chem. 14: 410-413.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Lu, P.-Y. and R. Metcalf. 1975. Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. Environ. Health Perspect. 19: 269-273.

Mackay, D. and P.J. Leinonen. 1975. Rates of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Morrison, H.A. 1979. The photochemistry of the nitro and nitroso groups. *In* The Chemistry of the Nitro and Nitroso Groups. H. Feuer (ed.). Interscience Publ., New York. pp. 165-212.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Pitter, P. 1976. Determination of biological degradability of organic substances. Water Res. 10: 231-235.

RIWA (Rijncommissie Waterleidingbedrijven). 1974. De samenstelling van het Rijn en Maaswater in 1974. Secretariaat RIWA, condensatorweg 54, Pb 8169. Amsterdam-Sloterwijk. (Cited in Verschueren 1983.)

Shackelford, W.M. and L.H. Keith. 1976. Frequency of Organic Compounds Identified in Water. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/4-76-062. 617 pp. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1979. Nitrobenzene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 79-1 to 79-8.

U.S. EPA. 1980. Ambient Water Quality Criteria for Nitrobenzene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-061.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.6.8 Nitrophenols

6.3.6.8.1 Uses and Production

Nitrophenols are mono-, di- and trinitro-derivatives of hydroxybenzene (phenol). The primary use of mononitrophenols is as intermediates for the production of dyes, pigments, pharmaceuticals, rubber chemicals, lumber preservatives, photographic chemicals and pesticidal and fungicidal agents. 4-Nitrophenol is used in the manufacture of ethyl and methylparathion (U.S. EPA 1980). An estimated (4.5-6.8) × 10^6 kg of 2-nitrophenol and less than 0.5 x 10^6 kg of 3-nitrophenol are produced annually in the U.S.A. Approximately 19 x 10^6 kg of 4-nitrophenol are produced annually in the U.S.A. (Howard *et al.* 1976; Hoecker *et al.* 1977; U.S. EPA 1980). 3-Trifluoromethyl-4-nitrophenol (TFM) is used as a lampricide to control the sea lamprey in the Great Lakes (NRCC 1985).

The U.S. production and consumption of 2,4-dinitrophenol are estimated at 4 × 10^5 and 5 × 10^5 kg·a^{-1}, respectively (U.S. International Trade Commission 1967-1973; Howard *et al.* 1976; U.S. EPA 1980). The production and usage of other dinitrophenol isomers are limited, and little information is available. 2,4-Dinitrophenol is used primarily as a chemical intermediate in the production of sulphur dyes, azo dyes, photochemicals, pest control agents, wood preservatives and explosives (Matsuguma 1967; U.S. EPA 1980).

2,4,6-Trinitrophenol, or picric acid, is used as a dye intermediate, explosive, analytical reagent, germicide, fungicide, staining agent and tissue fixative, tanning agent, photochemical agent, pharmaceutical and process material for the oxidation and etching of iron, steel and copper surfaces (Matsuguma 1967; U.S. EPA 1980).

Dinitrocresols have also received little study. The 4,6-isomer is the only one of six isomers that is of commercial importance. 4,6-Dinitrocresol is used primarily as a blossom-thinning agent on fruit trees and as a fungicide, insecticide and acaricide on fruit trees during the dormant season (U.S. EPA 1980).

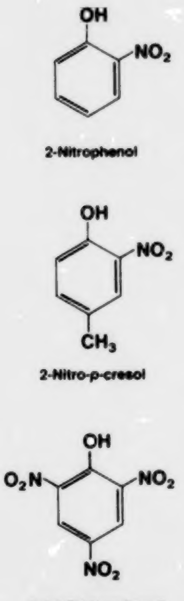
Nitrophenols (*o*-, *m*- and *p*-nitrophenol) are not produced in Canada. Importation and consumption of nitrophenols were 2 and 1-2 t for 1982 and 1983, respectively (CORPUS Information Services 1985). Nitrofen (nitrophen), a formulated herbicide, was not imported into Canada in 1981 and 1982. In 1981 and 1982, 394 and 270 t, respectively, of nitrated and nitrosated derivatives of phenols (group not specified), including dinitrophenols, were imported into Canada. Also in 1981 and 1982, 3 and 4 t, respectively, of picric acid (2,4,6-trinitrophenol) were imported into Canada. Other nitrophenols are imported into Canada, but individual values are unavailable because they do not appear in a separate category in the Statistics Canada (1983) publication. Information on production of nitrophenols in Canada is unavailable.

As of June, 1984, nitrophenols were on the List of Candidate Chemicals of the Environmental Contaminants Act. Further investigation on use patterns and environmental concentrations will determine whether the group should be included on the List of Priority Chemicals because of their toxicity to humans and the ecosystem (Environment Canada 1985).

6.3.6.8.2 Sources and Pathways for Entering the Aquatic Environment

Major routes of nitrophenol entry to the aquatic environment are through the industrial effluents of production plants and chemical firms where these compounds are used as intermediates. In a 1980-1981 survey of various contaminants in industrial effluents in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 µg·L^{-1} of 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and 2,6-dinitro-*o*-cresol) were observed in 13 samples (Environment Canada 1984). In a survey in 1979-1980 of the constituents in the final effluents from various petrochemical plants along the St. Clair River near Sarnia, Ontario, samples were analyzed for four nitrophenol compounds: 2-nitrophenol was detected in 1 of 2 samples, but the concentration was not measured; 4-nitrophenol was detected in 9 of 11 samples at a concentration range of 1-10 µg·L^{-1}; 2,4-dinitrophenol was detected in all 9 samples at a concentration range of 1-100 µg·L^{-1}; and 4,6-dinitro-*o*-cresol was detected in treated water (drinking water) at an estimated concentration between 10 and 100 µg·L^{-1} (Munro *et al.* 1985).

Agricultural runoff in areas where pesticides containing nitrophenols have been used will also release these compounds to water systems (U.S. EPA 1980). Since 3-trifluoromethyl-4-nitrophenol was first used in 1958 to control the sea lamprey, a total of about 9 x 10^5 kg has been applied directly to the streams of Lakes Superior, Michigan, Huron and Ontario (NRCC 1985).


2-Nitrophenol

2-Nitro-*p*-cresol

2,4,6-Trinitrophenol (picric acid)

Figure 6-7. Nitrophenols.

The microbial degradation or photodegradation of compounds containing some form of nitrophenol may also release nitrophenols to the environment. 4-Nitrophenol may be produced in the atmosphere through the photochemical reaction between benzene and nitrous oxide (U.S. EPA 1980).

6.3.6.8.3 Environmental Concentrations

Systematic monitoring of water for nitrophenols has rarely been carried out. In terms of the quantity produced and the potential for environmental contamination, the 4-nitrophenol isomer is probably the most important of the mononitrophenols. 4-Nitrophenol concentrations of 1.4 mg·L^{-1} in lagoon wastewater from a chemical plant (Webb *et al.* 1973) and 0.2 mg·L^{-1} in an Iowa water supply contaminated by coal gas plant residues have been found (Burnham *et al.* 1971). Little information exists on concentrations in Canadian waters, although it is likely that measurable amounts of mononitrophenols may be present in localized areas where organophosphate pesticides have been used. Sampling results for nitrophenols are not reported in NAQUADAT (1985). 4-Nitrophenol, 2,4-dinitrophenol and 4,6-dinitro-*o*-cresol were detected (1 µg·L^{-1}) in two samples taken from the St. Clair River. The concentrations for each nitrophenol were not measured, but were estimated to fall in the following ranges: 4-nitrophenol, 1-10 µg·L^{-1}; 2,4-dinitrophenol, 1-10 µg·L^{-1} for one sample and 1-10 mg·L^{-1} for the second sample; and 4,6-dinitrophenol, 1-100 µg·L^{-1} (Munro *et al.* 1985).

Table 6-100. Physical-chemical Properties of Some Nitrophenols

Compound	Molecular weight	Melting point (°C)	Boiling point (°C (kPa))	Vapour pressure (kPa (°C))	Water solubility (mg·L⁻¹ (°C))	Octanol/water partition coefficient (log P_{ow})[1]	Acidity constant (pK_a)[2]
2-Nitrophenol	139.11	45	214-217	2.7 (105)	2.1×10^3 (20)	1.76	7.21
3-Nitrophenol	"	96	194 (9)		1.3×10^4 (25)		
4-Nitrophenol	"	114	279 decomposes	0.3 (146)	1.6×10^4 (25)	1.91	7.15
2,4-Dinitrophenol	184.11	111-114			5.6×10^3 (18)	1.53	4.09
2-Nitro-*p*-cresol	153.13	36.5	125 (3.3)				
4,6-Dinitro-*m*-cresol	198.13	85.8					
2,4,6-Trinitrophenol	229.11	121.8	explodes >300°C		1.4×10^4 (20)	2.03	

[1] Leo *et al*. 1971.

[2] Pearce and Simpkins 1968.

Sources: U.S. EPA 1979; Verschueren 1983.

6.3.6.8.4 Forms and Fate in the Aquatic Environment

Nitrophenols (Figure 6-7), including mono-, di- and tri-nitrophenols and catechols, have, in general, low vapour pressures and high water solubilities (see Table 6-100) (U.S. EPA 1979; Verschueren 1983). Nitrophenols will occur to an appreciable extent in anionic form in environmental surface waters (pK_a 4-7) (Pearce and Simpkins 1968).

Very little information is available on the fate of nitrophenols in the aquatic environment. No one mechanism has been found which is responsible for the transport or removal of nitrophenols from surface waters, although photooxidation, sorption and biodegradation may remove some nitrophenols from the water column under certain conditions (Pearce and Simpkins 1968).

In general, nitrophenols have relatively low calculated octanol/water partition coefficients, and, hence, sorption by organic matter will not be significant in the aquatic environment (Leo *et al*. 1971). 4-Nitrophenol is strongly adsorbed by montmorillonite clay with little or no desorption (Saltzman and Yariv 1975). 2-Nitrophenol appears to be an effective flocculant for clays and soils in aqueous suspension (Chang and Anderson 1968). TFM may be adsorbed to sediments; the degree of sorption increases with organic matter content of the sediment (NRCC 1985).

Little information is available on the photolysis of nitrophenols in dilute aqueous solutions. 4-Nitrophenol (200 mg·L⁻¹) was degraded in aqueous solution within a period of 1-2 months when exposed to sunlight; hydroquinone and 4-nitrocatechol were identified as products (Nakagawa and Grosby 1974). Photoreduction of the nitro group of the nitrophenol may occur. The nitro group of nitrofen (niclofen, 2,4-dichlorophenyl-4-nitrophenyl ether) underwent photochemical reduction of the amino and azo groups in an aqueous solution containing 10% methanol (Nakagawa and Grosby 1974). The photolytic half-life of TFM in streams was estimated to be 3.5 d in spring, 3 d in summer and 5 d in autumn, assuming sunny weather and a stream depth of 55 cm (NRCC 1985).

Oxidation and hydrolysis reactions involving nitrophenols are not expected to be significant in the aquatic environment. It is also unlikely that nitrophenols will be volatilized from surface waters to any appreciable extent (Pearce and Simpkins 1968).

Few studies are available on the biodegradation of nitrophenols by natural communities of microorganisms. In general, nitrophenols appear to be more resistant to degradation than are other phenols (see Section 6.3.6.6). Mononitrophenols may, however, be degraded during activated sludge treatment. Dinitrophenols are resistant compared with mononitrophenols (Pitter 1976). Only 10% of 4,6-dinitro-*o*-cresol (207 mg·L⁻¹) was degraded by activated sewage sludge after a 48-h incubation (Cabridenc 1966). Microorganisms from soil, water and mud were unable to utilize 4-nitrophenol as a sole carbon source (Brebion *et al*. 1967). 3-Nitro- and 4-nitrophenol required a lag phase of 4 and 16 d, respectively, before being slowly degraded in the presence of natural communities of soil organisms. 2-Nitrophenol was not degraded after 64 d (Alexander and Lustigman 1966). TFM remained unaltered in the presence of microorganisms under aerobic conditions for periods as long as 80 d. In anaerobic environments, TFM was microbially reduced to 3-trifluoro-4-aminophenol in 5-20 d (NRCC 1985). Because nitrophenols have relatively low octanol/water partition coefficients, their bioaccumulation in most aquatic organisms is not expected to be significant (Pearce and Simpkins 1968). A bioconcentration factor of 180 was found for fathead minnows (*Pimephales promelas*) exposed to 1,4-dinitrophenol (~4 µg·L⁻¹) for 28 d. The biological half-life was found to be less than 7 d (Call *et al*. 1980). TFM does accumulate in some aquatic organisms such as sea lamprey and annelids; however, it is rapidly metabolized and excreted by invertebrates and teleosts (NRCC 1985).

6.3.6.8.5 References

Alexander, M. and B.K. Lustigman. 1966. Effect of chemical structure on microbial degradation of substituted benzenes. J. Agric. Food Chem. 14: 410-413.

Brebion, G., R. Cabridenc and B. Huriet. 1967. Studying the biodegradation possibilities of industrial effluents. Application to the biodegradation of phenols. Rev. Inst. Fr. Pet. Ann. Combust. Liq. 22: 1029-1052. (Cited in U.S. EPA 1979.)

Burnham, A.K., G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec and R. Illis. 1971. Identification and estimation of neutral organic contaminants in potable water. Anal. Chem. 44: 139-142. (Cited in U.S. EPA 1980.)

Cabridenc, R. 1966. Métabolisation du phénol et des produits phénoliques. *Dans* La Pollution des Eaux. Conférence Arts Chimiques, Paris, 1965. p. 119. (Cited in Verschueren 1983.)

Call, D.J., L.T. Brooke and P.-Y. Lu. 1980. Uptake, elimination and metabolism of three phenols by fathead minnows. Arch. Environ. Contam. Toxicol. 9: 699-714.

Chang, C.W. and J.U. Anderson. 1968. Flocculation of clays and soils by organic compounds. Soil Sci. Soc. Am. Proc. 32: 23-27. (Cited in U.S. EPA 1979.)

CORPUS Information Services. 1985. Nitrophenols (*o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol). CPI Product Profiles. Don Mills, Ontario. Prepared for Commercial Chemicals Branch, Environment Canada, Ottawa.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada. 1985. Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa.

Hoecker, J.E., P.R. Durkin, A. Hanchett, L.N. Davis and W.M. Meylan. 1977. Information Profiles on Potential Occupational Hazards. National Institute for Occupational Safety and Health, Cincinnati, Ohio. Rep. No. TR-77-565. (Cited in U.S. EPA 1980.)

Howard, P.H., J. Santodonato, J. Saxena, J. Malling and D. Greninger. 1976. Investigation of Selected Potential Environmental Contamination: Nitroaromatics. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA/560/2-76/010.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

Matsuguma, H.J. 1967. Nitrophenols. *In* Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 13. 2nd edition. E.A. Parolla, G.O. Schetty, F.L. Dankberg, J.J. Kerstein and L.L. Strauss (eds.). John Wiley & Sons, Toronto, Ontario. p. 888.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

Nakagawa, M. and D.G. Grosby. 1974. Photodecomposition of nitrofen. J. Agric. Food Chem. 22: 849-853.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1985. TFM and Bayer 73. Lampricides in the Aquatic Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 22488. 184 pp.

Pearce, P.J. and R.J.J. Simpkins. 1968. Acid strengths of some substituted picric acids. Can. J. Chem. 46: 241-248.

Pitter, P. 1976. Determination of biological degradability of organic substances. Water Res. 10: 231-235.

Saltzman, S. and S. Yariv. 1975. Infrared study of the sorption of phenol and *p*-nitrophenol by montmorillonite. Soil Sci. Soc. Am. Proc. 39: 474-479. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

U.S. EPA. 1979. 2-Nitrophenol. 4-Nitrophenol. 2,4-Dinitrophenol. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 88-1 to 88-9, 89-1 to 89-8, and 90-1 to 90-9.

U.S. EPA. 1980. Ambient Water Quality Criteria for Nitrophenols. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-063.

U.S. International Trade Commission. 1967-1973. Synthetic Organic Chemicals: U.S. Production and Sales. Washington, D.C. (Cited in U.S. EPA 1980.)

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Webb, R.G., A.W. Garrison, L.H. Keith and J.M. McGuire. 1973. Current Practices in GC-MS Analysis of Organics in Water. U.S. Environmental Protection Agency, Washington, D.C. EPA-R2-73-277.

6.3.6.9 Styrene

6.3.6.9.1 Uses and Production

Styrene is used in the manufacture of polystyrene plastics and resins, insulators, styrene-butadiene rubber and protective coatings (Verschueren 1983). Approximately 87% of the styrene consumed in the United States during 1976 was used in the production of plastics and resins, 11% for styrene-butadiene rubber and 2% for miscellaneous applications (NAS 1980).

Styrene is produced from ethylbenzene (NAS 1980). Styrene is currently produced in Sarnia, Ontario, and, since 1984, at Scotford, Alberta. Production, importation, consumption and exportation of styrene and three styrene compounds are presented in Table 6-101.

6.3.6.9.2 Sources and Pathways for Entering the Aquatic Environment

Styrene may enter the aquatic environment during its manufacture, use and disposal. Although few quantitative data are available, alkyl benzenes, which may include styrene and its derivatives, have been identified in some industrial effluents. Styrene has been found in the effluents from petroleum-refining (31 $\mu g \cdot L^{-1}$), chemical (30 $\mu g \cdot L^{-1}$), rubber (2.6-3 $\mu g \cdot L^{-1}$) and textile manufacturing plants in the United States (Shackelford and Keith 1976). Styrene may enter the atmosphere via evaporation and combustion. A laboratory study of the thermal degradation of polystyrene found that approximately 5-6% (by weight) of the starting material was decomposed to styrene, which was released as vapour and particles (Pfaffli *et al.* 1978). Once in the atmosphere, it is expected that styrene will be readily photooxidized (see Section 6.3.6.9.4). Some styrene may enter water and soil from discarded products in landfills and chemical waste dumps, although no quantitative data are available (NAS 1980). Styrene was detected in the final effluent of a Canadian organic chemical plant at a concentration of 500 $\mu g \cdot L^{-1}$ (detection limit 0.2 $\mu g \cdot L^{-1}$) in 1985 (Sigma Resource Consultants Ltd. 1985). In 1977, a study conducted on industrial outfalls in the Sarnia (St. Clair River) area found that only one sample of many collected from 26 sites contained styrene, at a concentration of 200 $\mu g \cdot L^{-1}$ (Duholke and Meresz 1977).

6.3.6.9.3 Environmental Concentrations

Styrene has been detected in Cleveland's water supply and in a discharge to the St. Clair River (IJC 1981). Residues of chlorinated styrenes have been found in fish and birds of the Great Lakes. Octachlorostyrene residues were found in 13 of 17 fish samples from Lakes Huron, Erie, Ontario and St. Clair, in concentrations ranging from 2.0 $ng \cdot g^{-1}$ (whole fish wet weight) in Saginaw Bay, Lake Huron, to 405 $ng \cdot g^{-1}$ in northern pike taken from Ashtabula River, Ohio, where the river empties into Lake Erie. Although octachlorostyrene is not a commercial product, it may be formed by high temperature carbon/chlorine reactions (Kuehl *et al.* 1981). A study conducted in 1978 reported that styrene was found in U.S. waters at concentrations of 0.13-80 $\mu g \cdot L^{-1}$ in surface water and 0.01-

Table 6-101. Production, Consumption, Importation and Exportation of Styrene and Three Styrene Compounds in Canada

Compound	Year	Amount (kt) Production	Consumption	Importation	Exportation
Styrene	1983	306.5	216.5		90.0
	1984	350	233		117
Polystyrene	1983	135	136.9	31.1	21.2
	1984	141	144.4	30	26.6
Styrene-butadiene latices	1983	42.3	42	18.3	20
	1984	44	43.8	15	15
Styrene-butadiene rubber	1983	94.5	80.3	24.7	16
	1984	90	85.4	18	22.5

Source: CORPUS Information Services 1984.

0.05 $\mu g \cdot L^{-1}$ in tap water (Waggot and Wheatland 1978). Sampling results for styrene are not reported in NAQUADAT (1985).

6.3.6.9.4 Forms and Fate in the Aquatic Environment

Styrene (ethenylbenzene, vinylbenzene) (Figure 6-8) is an odourless liquid of molecular weight 104.14; it has a boiling point of 145.2°C at 101 kPa, a vapour pressure of 70 Pa at 20°C, a water solubility of 280 $mg \cdot L^{-1}$ at 15°C and a calculated log octanol/water partition coefficient of 2.95 (NAS 1980; Verschueren 1983; WHO 1983).

Very little information is available on the fate of styrene (or chlorinated styrenes) in the aquatic environment (NAS 1980).

Some sorption of styrene to organic matter in the aquatic environment may occur. Based on information on other alkylbenzenes, such as toluene (see Section 6.3.6.10) and ethylbenzene (see Section 6.3.6.5), oxidation, microbial degradation and bioaccumulation are not expected to be significant. Hydrolysis of styrene, which has a half-life of 10^7 d at pH 5, is not expected to be important in the aquatic environment (Wolfe 1980).

Like other low-molecular-weight alkylbenzenes, styrene is expected to be readily volatilized from surface waters. Volatilization half-lives of 5-6 h have been estimated for ethylbenzene, a similar compound (Mackay and Leinonen 1975) (see Section 6.3.6.5). Once in the atmosphere, styrene will be degraded through free-radical chain reactions, involving the hydroxyl radical. Unlike alkylbenzenes that have saturated side chains, styrene will also react rapidly with ozone. Although data are not available for styrene, the half-life of ethylbenzene and *n*-propylbenzene in the atmosphere has been estimated to be 50 h. It is expected that the half-life of styrene will be shorter (NAS 1980).

6.3.6.9.5 References

CORPUS Information Services. 1984. Styrene. Styrene-butadiene latices. Styrene-butadiene rubber. Polystyrene. CPI Product Profiles. Don Mills, Ontario.

Duholke, W.K. and O. Meresz. 1977. Organic Compounds of Industrial Origin in the St. Clair River. Ontario Ministry of the Environment, Toronto, Ontario. Rep. No. OTC/MS-7507.

IJC. 1981. Annual Report. Committee on the Assessment of Human Health Effects of Great Lakes Water Quality. Report to the Great Lakes Water Quality Board/Great Lakes Science Advisory Board, International Joint Commission, November. 142 pp.

Kuehl, D.W., K.L. Johnson, B.C. Butterworth, E.N. Leonard and G.D. Veith. 1981. Quantification of octachlorostyrene and related compounds in Great Lakes fish by gas chromatography-mass spectrometry. J. Great Lakes Res. 7: 330-335.

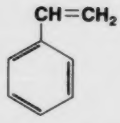


Figure 6-8. Styrene.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1980. The Alkyl Benzenes. Committee on Alkyl Benzene Derivatives. National Academy Press, U.S. National Academy of Sciences, Washington, D.C.

Pfaffli, P., A. Zitting and H. Vainio. 1978. Thermal degradation products of homopolymer polystyrene in air. Scand. J. Work Environ. 4 (Suppl. 2): 22-27.

Shackelford, W.M. and L.H. Keith. 1976. Frequency of Organic Compounds Identified in Water. Office of Research and Development, Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/4-76-062. (Cited in NAS 1980.)

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Waggot, S. and H. Wheatland. 1978. Contribution of Different Sources to Contamination of Surface Waters with Specific Persistent Organic Pollutants. *In* 2nd Int. Symp. Aquatic Pollutants: Transformation and Biological Effects, Sept. 1977, Amsterdam, The Netherlands. Pergamon Press, New York. pp. 141-168.

WHO. 1983. Styrene. Environmental Health Criteria 26. World Health Organization, Geneva. 123 pp.

Wolfe, N.E. 1980. Determining the role of hydrolysis in the fate of organics in natural waters. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 163-178.

6.3.6.10 Toluene

6.3.6.10.1 Uses and Production

Toluene (toluol, methylbenzene, phenylmethane) is used in the production of benzene, benzoic acid, phenol, trinitrotoluene, lacquers, resin solutions, lacquer thinners, as a gasoline component and as a solvent in formulations of rubber cements, paints, inks and pesticides (Environment Canada 1984a). In 1982, 39% of toluene in Canada was used for

Table 6-102 Production, Consumption, Importation and Exportation of Toluene in Canada

Parameter	Amount (kt) 1983	1984
Production	410.6	430.5
Consumption	156.0	186.0
Importation	3.5	1.5
Exportation	238.0	246.0

Source: CORPUS Information Services 1985.

solvents, 25% for benzene production and 22% for benzoic acid/phenol production (Environment Canada 1984a).

Toluene is primarily produced in Canada by catalytic reformation of naphthene-rich petroleum feedstock fractions, generally in conjunction with the manufacture of benzene and xylenes. Current Canadian production occurs in Quebec, Ontario and British Columbia. Domestic production in 1982 was 470 x 10^3 t, and importation was 1.1 x 10^3 t (Environment Canada 1984a). Production, importation, consumption and exportation of toluene in Canada are presented in Table 6-102.

6.3.6.10.2 Sources and Pathways for Entering the Aquatic Environment

Sources of toluene in the aquatic environment include industrial effluents, spills, discharges of oil and gas from boats, municipal waste treatment facilities, agricultural runoff, landfills and atmospheric deposition (U.S. EPA 1980).

Toluene was detected in the total effluent of a Canadian organic chemical plant at a concentration of 3.6 $\mu g \cdot L^{-1}$ (detection limit 0.2 $\mu g \cdot L^{-1}$) (Sigma Resource Consultants Ltd. 1985). Toluene was detected in the final effluents of four organic chemical industries that discharge into the St. Clair River, at a concentration range of 1-100 $\mu g \cdot L^{-1}$ based on 37 samples taken in 1979 and 1980 (Munro *et al.* 1985). Total Ontario municipal and industrial trace contaminant loadings to the Niagara River and its tributaries have been estimated at less than 0.485 $kg \cdot d^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981).

In a 1980 survey of the constituents of industrial and municipal effluents at Cornwall, Ontario, toluene was reported in 38 of 45 samples at concentrations ranging from trace (<1-5 $\mu g \cdot L^{-1}$) to 41.3 $\mu g \cdot L^{-1}$. A storm sewer sample had a toluene concentration of 678 $\mu g \cdot L^{-1}$. Total toluene loadings from 14 industrial and municipal outfalls to the St. Lawrence River at Cornwall, Ontario, were estimated at 2.29 $kg \cdot d^{-1}$ (Environment Canada 1984b).

An estimated 691 800 t of toluene are discharged annually to the U.S. environment by industry. Of the toluene released, 99.3% (686 960 t) is in the form of atmospheric emissions, and the remaining 0.7% (4840 kg) is in wastewater (U.S. EPA 1980).

6.3.6.10.3 Environmental Concentrations

Concentration ranges for toluene detected in surface water at treatment plant intakes of cities along the upper Niagara River during 1979 and 1980 surveys are presented in Table 6-103. Toluene was detected in three of nine samples taken in 1980 from the surface waters of the St. Lawrence River at Cornwall, Ontario, at trace (<1-5 $\mu g \cdot L^{-1}$) concentrations. A Cornwall drinking water sample taken in 1980 contained trace (<1-5 $\mu g \cdot L^{-1}$) concentrations of toluene (Environment Canada 1984b). Sampling results for toluene are not reported in NAQUADAT (1985).

Table 6-103. Surface Water Concentration Ranges for Toluene at Four Sites Along the Upper Niagara River in 1979 and 1980

Sample site	Year	Number of samples	Number of detectable samples	Concentration range ($\mu g \cdot L^{-1}$)
Niagara-on-the-Lake	1979	9	3	ND[1]-0.049
	1980	14	5	ND-0.3
Niagara Falls	1979	9	7	ND-0.3
	1980	13	7	ND-0.1
Fort Erie	1979	9	4	ND-2.9
	1980	13	6	ND-0.1
St. Catharines	1980	8	3	ND-0.1

[1] ND = not detected (detection limit is not specified, but in general is in the range of 0.2-0.5 $\mu g \cdot L^{-1}$).

Source: Environment Canada/Ontario Ministry of the Environment 1981.

Toluene has been detected in 14 of 17 water supplies in the United States in concentrations below 1 $\mu g \cdot L^{-1}$. Concentrations of toluene in a raw water sample and in 3 of 11 finished waters in the United States ranged from 0.5 to 17 $\mu g \cdot L^{-1}$ (NAS 1980). Toluene has been detected at trace concentrations (<1.5 $\mu g \cdot L^{-1}$) in Great Lakes water and at concentrations as high as 58 $\mu g \cdot L^{-1}$ in the Niagara River (IJC 1981). Benzaldehyde and benzoic acid, both toluene metabolites, have been found at concentrations up to 19 $mg \cdot L^{-1}$ in finished water (U.S. EPA 1980).

6.3.6.10.4 Forms and Fate in the Aquatic Environment

Toluene (Figure 6-9) is a volatile, colourless liquid with a water solubility of 534.8 ± 9 $mg \cdot L^{-1}$ at 25°C (Sutton and Calder 1975) and a vapour pressure of 4.0 kPa at 26°C (Weast 1977). Little information is available on the aquatic environmental fate of toluene. As is the case for other low-molecular-weight aromatic hydrocarbons (e.g. benzene), the major removal mechanism for toluene is volatilization with subsequent atmospheric oxidation (U.S. EPA 1979).

No specific environmental data on sorption of toluene are available; some adsorption to organic-rich sediments is, however, anticipated (U.S. EPA 1979) (log $P_{ow} = 2.69$; Tute 1971).

Oxidation of toluene in aqueous systems is not expected. As well, hydrolysis probably does not contribute to the loss of toluene from the water column (U.S. EPA 1979).

The half-life of toluene as a result of its volatilization from a water column 1 m in depth has been estimated to be approximately 5 h (Mackay and Leinonen 1975). Based on smog chamber studies (Altshuller *et al.* 1962; Laity *et al.* 1973), the atmospheric half-life of toluene is estimated at approximately 15 h (U.S. EPA 1979).

Several species of bacteria isolated from soil can utilize toluene as a sole carbon source under laboratory conditions (Claus and Walker 1964; Gibson *et al.* 1966). However, little

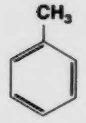


Figure 6-9. Toluene.

information is available on toluene biodegradation in natural systems (U.S. EPA 1979). Toluene, which has a log octanol/water partition coefficient of 2.69 (Tute 1971), may be accumulated to some extent under conditions of continuous exposure. In one study, toluene was rapidly taken up by Pacific herring (*Clupea harengus pallasi*), reaching maximum tissue levels within 24 h. The gallbladder had the highest tissue levels, with a concentration factor of 240. However, depuration was rapid; no toluene was detectable in most tissues (except gallbladder, intestine and pyloric ceca) 1-2 d after termination of exposure (Korn *et al.* 1977). Eels (*Anguilla japonica*) reared in seawater containing crude oil suspensions (50 $mg \cdot L^{-1}$) accumulated toluene (concentration factor 13.2 at 10 d). Upon transfer to clean seawater, the half-life for depuration was 1.4 d (Ogata and Miyake 1979).

6.3.6.10.5 References

Altshuller, A.P., I.R. Cohen, S.F. Sleva and S.L. Kopczynski. 1962. Air pollution: photooxidation of aromatic hydrocarbons. Science 138: 442-443.

Claus, D. and N. Walker. 1964. The decomposition of toluene by soil bacteria. J. Gen. Microbiol. 36: 107-122.

CORPUS Information Services. 1985. Toluene. CPI Product Profiles. Don Mills, Ontario.

Environment Canada. 1984a. Toluene. Environmental and Technical Information for Problem Spills (EnviroTIPS). Technical Services Branch, Environmental Protection Programs Directorate, Environmental Protection Service, Ottawa. 104 pp.

Environment Canada. 1984b. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Gibson, D.T., J.R. Koch and R.E. Kallio. 1966. Oxidative degradation of aromatic hydrocarbons by microorganisms. Enzymatic formation of catechol from benzene. Biochemistry 7: 2653-2662. (Cited in U.S. EPA 1979.)

IJC. 1981. Annual Report. Committee on the Assessment of Human Health Effects of Great Lakes Water Quality. Report to the Great Lakes Water Quality Board/Great Lakes Science Advisory Board, International Joint Commission, November. 142 pp.

Korn, S., N. Hirsch and J.W. Struhsaker. 1977. The uptake, distribution and depuration of ^{14}C-benzene and ^{14}C-toluene in Pacific herring, *Clupea harengus pallasi*. U.S. Natl. Mar. Fish. Serv., Fish. Bull. 75: 633-636.

Laity, J.L., I.G. Burstain and B.R. Appel. 1973. Photochemical smog and the atmospheric reactions of solvents. *In* Solvents, Theory and Practice. R.W. Tess (ed.). Adv. Chem. Ser. No. 124. pp. 95-112. (Cited in U.S. EPA 1979.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1980. The Alkyl Benzenes. Committee on Alkyl Benzene Derivatives. National Academy of Sciences, U.S. National Research Council, Washington, D.C.

Ogata, M. and Y. Miyake. 1979. Disappearance of aromatic hydrocarbons and organic sulfur compounds from fish flesh reared in crude oil suspension. Water Res. 13: 75-78.

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

Sutton, C. and J.A. Calder. 1975. Solubility of alkylbenzenes in distilled water and sea water at 25°C. J. Chem. Eng. Data 20: 320-322.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 5: 1-77.

U.S. EPA. 1979. Toluene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 80-1 to 80-7.

U.S. EPA. 1980. Ambient Water Quality Criteria for Toluene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-075.

Weast, R.C. (ed.). 1977. CRC Handbook of Chemistry and Physics. CRC Press, Inc., Cleveland, Ohio. 2398 pp. (Cited in U.S. EPA 1979.)

6.3.7 Nitrilotriacetic Acid

6.3.7.1 Uses and Production

The trisodium salt of nitrilotriacetic acid (NTA) is used in a variety of industrial and domestic applications because of its chelating properties, and as a builder to replace phosphates in detergents. It is also used as an eluting agent in the purification of rare earth elements (Verschueren 1983). In Canada, the principal use of NTA is in laundry detergents, which contain approximately 15% NTA. It is also used in paper and cellulosic production, metal plating, textile manufacturing, photography, cleaning operations and other applications where a chelating agent is required (Prakash 1976; Health and Welfare Canada 1980; Anderson *et al.* 1985).

NTA production is limited in Canada; most of the NTA used is imported from the U.S.A. (Health and Welfare Canada 1980). Importation of NTA is presented in Table 6-104.

In 1977, the Canadian consumption of NTA was estimated to be 27 200 t (IJC 1977).

6.3.7.2 Sources and Pathways for Entering the Aquatic Environment

The main route by which NTA enters the aquatic environment is liquid effluents (McNeely *et al.* 1979). Activated sludge systems may degrade 80-100% of NTA under optimum conditions. In winter, the degradation is less efficient, with 65-85% degradation (Health and Welfare Canada 1980).

6.3.7.3 Environmental Concentrations

The concentration of NTA in most surface waters is usually low, mainly because of dilution and degradation in receiving

Table 6-104. Importation of Nitrilotriacetic Acid and Its Sodium Salt into Canada

Compound	Amount (t) 1981	1982	1983
Nitrilotriacetic acid	194	14	NA[1]
Sodium nitrilotriacetate (sodium salt of NTA)	22 571	18 667	19 541

[1] NA = not available.

Sources: Statistics Canada 1983, 1984.

Table 6-105. Environmental Concentration Ranges for Nitrilotriacetic Acid in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<0.01-0.06	179	Prior to 1980
Western	<0.01-0.29	387	Prior to 1980
Central	0.0001-3.9	2073	Prior to 1980
Atlantic	<0.01-0.025	93	Prior to 1980

[1] Detection limit is 0.1 $\mu g \cdot L^{-1}$.

Source: NAQUADAT 1985.

waters (Shannon *et al.* 1974). In Canada, the NTA concentrations of influents and effluents of treatment plants, as well as the receiving water above and below effluent outfalls, average 50 $\mu g \cdot L^{-1}$ (McNeely *et al.* 1979).

NTA has not been detected in Lake Ontario since July 1972 (detection limit 10 $\mu g \cdot L^{-1}$). None of 35 samples from the Canadian side of Lake Ontario, in 1975, contained NTA at or above 10 $\mu g \cdot L^{-1}$ (Matheson 1977). In the St. Lawrence River system, NTA concentrations between 10 and 30 $\mu g \cdot L^{-1}$ have been detected in the Montreal metropolitan area (Matheson 1977). In 1975, surveys of NTA in treated municipal waters across Canada showed that 88% of the samples had no detectable NTA. Only 23 localities had NTA concentrations higher than 10 $\mu g \cdot L^{-1}$; 16 of these were located in Quebec (Matheson 1977). Environmental concentration ranges for NTA in Canadian surface waters are presented in Table 6-105.

A survey of NTA concentrations in Canadian drinking water for 1972-1979 showed a range of <0.2-30 $\mu g \cdot L^{-1}$, and an average value of 2.8 $\mu g \cdot L^{-1}$; for raw water, values ranged from 0.2 to 33.5 $\mu g \cdot L^{-1}$, with a mean of 3.9 $\mu g \cdot L^{-1}$ (Malaiyandi *et al.* 1979). In a survey of 21 private wells, only one water sample had an NTA concentration (16.9 $\mu g \cdot L^{-1}$) above the limit of detection (McNeely *et al.* 1979).

6.3.7.4 Forms and Fate in the Aquatic Environment

NTA ($N(CH_2COOH)_3$) is a white, crystalline powder with a molecular weight of 191.14 and a melting point of 240°C. It is soluble in water (1.28×10^3 $mg \cdot L^{-1}$) and has a pK_1 of 3.03, pK_2 of 3.07 and pK_3 of 10.70 at 20°C (Vershueren 1983).

NTA may be readily biodegraded under aerobic conditions and at moderate temperatures. Under optimal conditions, and after a few weeks of acclimation, activated sludge systems are able to degrade 80-100% of the NTA load. At less favourable (wintertime) temperatures, degradation rates range from 65 to 85% (Rudd and Hamilton 1972; Eden *et al.* 1972; Rudd *et al.* 1973; Renn 1974; Moore and Barth 1976; Prakash 1976). Under low temperature and low oxygen conditions, however, biodegradation of NTA may be almost negligible. Receiving waters may also degrade NTA. Under summertime conditions and using effective sewage treatment, NTA was not detected in receiving waters; however, some NTA was detected at lower temperatures (Warren and Malec 1972).

NTA is biodegraded to ammonia, nitrate, carbon dioxide and water. The production of ammonia as a result of NTA degradation could lead to an increase of nitrate (by nitrification) in water (see Section 6.2.29.4). It has been theorized that NTA could biodegrade to secondary amines which could undergo nitrosification to form nitrosamines; these compounds, however, have not been found in either experimental studies or field surveys. Decarboxylation of NTA to secondary amines is also not considered likely to occur (Health and Welfare Canada 1980).

In view of the chelating properties of NTA, concern has focused on NTA – heavy metal relationships in the aquatic environment. The increased mobilization of heavy metals, such as iron, manganese, lead, zinc, copper and nickel, has been demonstrated (Chau and Shiomi 1972; Barica *et al.* 1973; Sanchez and Lee 1973). The degradation of NTA-metal complexes is generally greater in hard than in soft waters (Bjorndal *et al.* 1972). Complexes of iron, copper and cobalt are known to undergo photooxidation in the aquatic environment (Trott *et al.* 1972; Langford *et al.* 1973).

6.3.7.5 References

Anderson, R.L., W.E. Bishop and R.L. Campbell. 1985. A review of the environmental and mammalian toxicology of nitrilotriacetic acid. CRC Crit. Rev. Toxicol. 15: 1-102.

Barica, J., M.P. Stainton and A.L. Hamilton. 1973. Mobilization of some metals in water and animal tissue by NTA, EDTA and TPP. Water Res. 7: 1791-1804.

Bjorndal, H., H.O. Bouveng, P. Solyom and J. Werner. 1972. NTA in sewage treatment. Vatten 28: 5-16.

Chau, Y.K. and M.T. Shiomi. 1972. Complexing properties of nitrilotriacetic acid in the lake sediment. Water Air Soil Pollut. 1: 149-164.

Eden, G.E., G.E. Culley and R.C. Rootham. 1972. Effect of temperature in the removal of NTA (nitrilotriacetic acid) during sewage treatment. Water Res. 6: 877-883.

Health and Welfare Canada. 1980. Nitrilotriacetic acid. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 433-449.

IJC. 1977. A Report to the Great Lakes Research Advisory Board of the International Joint Commission on the Health Implications of NTA. Windsor, Ontario.

Langford, C.H., M. Wingham and V.S. Sastri. 1973. Ligand photooxidation in copper II complexes of nitrilotriacetic acid. Implications for natural waters. Environ. Sci. Technol. 7: 820-822.

Malaiyandi, U., D.T. Williams and R. O'Grady. 1979. National survey of nitrilotriacetic acid in Canadian drinking water. Environ. Sci. Technol. 13: 59-62.

Matheson, D.H. 1977. Nitrilotriacetic Acid (NTA) in the Canadian Environment. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. Sci. Ser. No. 74. 46 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Nitrilotriacetic acid. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 29-30.

Moore, L. and E.F. Barth. 1976. Degradation of NTA during anaerobic digestion. J. Water Pollut. Control Fed. 48: 2406-2409.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Prakash, A. 1976. NTA (Nitrilotriacetic Acid) – An Ecological Appraisal. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15023. 46 pp.

Renn, C.E. 1974. Biodegradation of NTA detergents in a wastewater system. J. Water Pollut. Control Fed. 46: 2363-2371.

Rudd, J.W.M. and R.D. Hamilton. 1972. Biodegradation of trisodium nitrilotriacetate in a model aerated sewage lagoon. J. Fish. Res. Board Can. 29: 1203-1208.

Rudd, J.W.M., B.E. Townsend and R.D. Hamilton. 1973. Discharge of nitrilotriacetic acid (NTA) from two sewage treatment facilities in a mid-continental climate. J. Fish. Res. Board Can. 30: 1026-1030.

Sanchez, I. and G.F. Lee. 1973. Sorption of copper on Lake Monona sediments. Effect of NTA on copper release from sediments. Water Res. 7: 587-593.

Shannon, E.E., P.S.A. Fowlie and R.J. Rush. 1974. A Study of Nitrilotriacetic Acid (NTA) Degradation in a Receiving Stream. Wastewater Technology Centre, Environmental Protection Service, Environment Canada. Rep. No. EPS 4-WP-74-7. 25 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Trott, T., R.W. Henwood and C.H. Langford. 1972. Sunlight photochemistry of ferric nitrilotriacetate complexes. Environ. Sci. Technol. 6: 367-368.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Warren, C.B. and E.J. Malec. 1972. Biodegradation of nitrilotriacetic acid and related imino and amino acids. Science 176: 277-279.

6.3.8 Nitrosamines

6.3.8.1 Uses and Production

N-nitrosodimethylamine has been used in the past as an industrial solvent (a use now abandoned), and is currently used as an intermediate in the synthesis of the rocket fuel, 1,1-dimethylhydrazine. Nitrosamines have potential uses as solvents in the fibre and plastics industry; antioxidants in fuels; additions to fertilizers; softeners for copolymers; synergists to self-extinguishing agents used in expanded polymer materials; insect repellants; insecticides, fungicides and bactericides; and lubricating oils (U.S. EPA 1977). Diphenylnitrosamine (which to date has not been found to be carcinogenic) is used as a vulcanizing retarder, and dinitrosopentamethylenetetramine is used as a blowing agent in the production of microcellular rubber (U.S. EPA 1977).

Canada imported 2 and 28 t of dimethylnitrosamine in 1981 and 1982, respectively (Statistics Canada 1983).

Nitrosamines may be formed in the environment or *in vivo* in animals via the interaction of nitrosating agents and secondary amines. In the presence of nitrite, there is a potential for the formation of nitrosamines (U.S. EPA 1977; NAS 1978). The formation of nitrosamines is dependent upon the pH of the aqueous medium. Nitrosation of dimethylamine reaches a maximum in the range of pH 3-4 (Mirvish 1970). However, dimethylnitrosamine has been formed from dimethylamine and nitrite at pH values as high as pH 7.7 in samples of soil, sewage and lake water (Mills and Alexander 1976).

6.3.8.2 Sources and Pathways for Entering the Aquatic Environment

Some nitrosamines and other *N*-nitroso compounds are discharged into the environment by human activities such as the fertilizer industry, sewage output and animal feedlots where nitrogen compounds are used. These compounds may also be formed in the air, water, soil or *in vivo* in animals when the appropriate amine and nitrite precursors are present (U.S. EPA 1977; NAS 1978).

6.3.8.3 Environmental Concentrations

No Canadian data are available on concentrations of nitrosamines in water. One study reported the occurrence of nitrosamines in a reservoir in Russia, but no concentrations were given (Shabad and Il'nitskii 1972). Concentrations of nitrosamines in water appear to be at or below the detection limits of available techniques. Water processed at a Munich, Germany, clarification plant contained less than 0.1 $\mu g \cdot L^{-1}$ of nitrosamines. Sediments from a nearby lake and river also contained less than 0.1 $\mu g \cdot kg^{-1}$ (Dure *et al.* 1975). Drinking water samples taken in the New Orleans area had concentrations estimated to be less than 0.1 $\mu g \cdot L^{-1}$ (Fine *et al.* 1975). Concentrations of below 0.015 $\mu g \cdot L^{-1}$ for volatile and non-volatile nonionic nitrosamines were reported in 12 rural well water samples taken in Illinois and Texas (Fine 1975). A rain-water puddle near a dimethylhydrazine plant in Baltimore contained 6000 $\mu g \cdot L^{-1}$ of dimethylnitrosamine (Fine 1975). A sample from a drainage ditch on the border of the property contained 5.9 $\mu g \cdot L^{-1}$, and water samples from the adjacent cove contained 0.26-0.94 $\mu g \cdot L^{-1}$ (Fine 1975). No data on nitrosamine concentrations in Canadian surface waters are available.

6.3.8.4 Forms and Fate in the Aquatic Environment

Simple dialkylnitrosamines ($RR' - N - N = O$, where R and R' refer to alkyl groups) are not readily degraded in sewage, soil or lake water, and are, therefore, considered to be relatively persistent in natural environments (Tate and Alexander 1976). Dialkylnitrosamines, such as dimethyl- and di-*n*-propylnitrosamine, are quite soluble in water (up to 9900 $mg \cdot L^{-1}$ for di-*n*-propylnitrosamine) (Mirvish *et al.* 1976), and are expected to be transported primarily in the soluble phase in the aquatic environment (U.S. EPA 1979).

Little sorption is expected to occur, at least for the dialkylnitrosamines, because they are water-soluble and have low organic partitioning characteristics (log octanol/water partition coefficients approximate 1) (Radding *et al.* 1977; U.S. EPA 1979). Diarylnitrosamines, such as diphenylnitrosamine, are expected to have a higher affinity for organic material (U.S. EPA 1979).

Dialkylnitrosamines are relatively stable towards photolysis in neutral aqueous solutions (Chow 1964; Burgess and Lavanish 1964), although slow photolytic decomposition of dimethylnitrosamine (74 $mg \cdot L^{-1}$) in aerated, distilled water has been demonstrated (half-life of 79 h) (Polo and Chou 1976).

Under acidic conditions, photolysis may be more rapid. Dimethylnitrosamine (300 mg·L^{-1}) had a half-life of 3 h in acidic water (pH not specified) when exposed to sunlight (MacNaughton and Stauffer 1975).

Oxidation, hydrolysis and volatilization are not expected to be significant in the aquatic environment (U.S. EPA 1979). Dimethyl- and di-*n*-propylnitrosamine were not degraded in lake water after 3.5 months (Tate and Alexander 1976). Although slowly degraded in sewage, these compounds were not degraded in anaerobic bog sediments. In addition, a lag of approximately 1 month was required for decomposition in soil (Tate and Alexander 1976). Because they have little tendency to partition towards lipophilic material, dialkylnitrosamines are not expected to bioaccumulate or biomagnify in the aquatic environment (U.S. EPA 1979).

6.3.8.5 References

Burgess, E.M. and J.M. Lavanish. 1964. Photochemical decomposition of N-nitrosamines. Tetrahedron Lett. 20: 1221-1226.

Chow, Y.L. 1964. Photolysis of N-nitrosamines. Tetrahedron Lett. 34: 2333-2338.

Dure, G., L. Weil and K.E. Quentin. 1975. Determination of nitrosamines in natural water and waste water. Z. Wasser Abwasser Forsch. 8(1): 20-30. (Chem. Abstr. 83(4): 32828F.) (Cited in U.S. EPA 1977.)

Fine, D.H. 1975. N-Nitrosamines in Urban Community Air. Progress Report. Prepared by Thermo Electron Research Center, Waltham, Massachusetts. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Contract No. 68-02-2363. (Cited in U.S. EPA 1977.)

Fine, D.H., D.P. Rounbehler, N.M. Belcher and S.S. Epstein. 1975. N-nitroso compounds in the environment. Paper presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada. (Cited in U.S. EPA 1977.)

MacNaughton, M.G. and T.B. Stauffer. 1975. The evaporation and degradation of N-nitrosodimethylamine in aqueous solutions. Air Force Civil Engineering Center, Environics Directorate. Kirkland Air Force Base, New Mexico. AFCEC-TR-75-9. 18 pp. (Cited in U.S. EPA 1979.)

Mills, A.L. and M. Alexander. 1976. Factors effecting dimethylnitrosamine formation in samples of soil and water. J. Environ. Qual. 5: 437-446.

Mirvish, S.S. 1970. Kinetics of dimethylamine nitrosation in relation to nitrosamine carcinogenesis. J. Natl. Cancer Inst. 44: 633-639.

Mirvish, S.S., P. Issenberg and H.C. Sornson. 1976. Air-water and ether-water distribution of N-nitroso compounds: implications for laboratory safety, analytical methodology and carcinogenicity for the rat esophagus, nose and liver. J. Natl. Cancer Inst. 56: 1125-1129.

NAS. 1978. Nitrates: An Environmental Assessment. National Academy of Sciences, Washington, D.C. 723 pp.

Polo, J. and Y.L. Chou. 1976. Efficient photolytic degradation of nitrosamines. J. Natl. Cancer Inst. 56: 997-1001.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. 147 pp.

Shabad, L.M. and A.P. Il'nitskii. 1972. Contamination of reservoirs by carcinogenic hydrocarbons. VOP Profil Zagrejazneniya Uhnesh Sredy. Chastnosti Vodocmov. Kanterogen Veshchesto. pp. 5-13. (Cited in U.S. EPA 1977.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tate, R.L., III and M. Alexander. 1976. Resistance of nitrosamines to microbial attack. J. Environ. Qual. 5: 131-133.

U.S. EPA. 1977. Scientific and Technical Assessment Report on Nitrosamines. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA-600/6-77-001.

U.S. EPA. 1979. Dimethylnitrosamine. Diphenylnitrosamine. Di-*n*-propylnitrosamine. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 99-1 to 99-7, 100-1 to 100-5, and 101-1 to 101-7.

6.3.9 Organic Carbon

6.3.9.1 Introduction

Organic carbon is composed of both dissolved and particulate forms. Total organic carbon (TOC) is often calculated as the difference between total carbon (TC) and total inorganic carbon (TIC). Lakes and rivers have approximately 10 times more dissolved inorganic matter than organic matter, whereas groundwaters have 100 times more inorganic matter than organic matter. Inorganic matter in seawater is 30 000 times more concentrated than organic matter. In contrast, swamps, marshes and bogs have much higher organic matter content (Thurman 1985). TOC has a direct relationship with both the biochemical (BOD) and chemical (COD) oxygen demands, and varies with the composition of organic matter present in the water (McNeely *et al.* 1979). Relatively little information is available on the broad classes or types of organic carbon that occur naturally in surface waters. Organic matter in soils, aquatic vegetation and aquatic organisms are major sources of organic carbon (Faust and Aly 1981).

Carbon is the most abundant element found in all organisms. Carbon compounds are the energy sources for heterotrophic organisms. The availability and rate of supply of specific forms of carbon (CO_2, HCO_3^-, CO_3^{2-}) regulate the extent and rate of biological activity (Wetzel 1975).

Plant photosynthesis is generally the major source of production of organic carbon in aquatic ecosystems; bacterial fixation contributes to a lesser degree. Approximately 6% of the total carbon of some heterotrophic bacteria comes from carbon dioxide (CO_2) fixation. For bacteria inhabiting deep oligotrophic waters, the carbon comes solely from carbon dioxide fixation. In deep oligotrophic reservoirs, heterotrophic bacterial CO_2 assimilation accounts for 24% of the total production of organic matter. Although the organisms cannot utilize the gas as a sole source of carbon, it has been shown to be essential for the growth of many heterotrophic bacteria (NAS 1977).

6.3.9.2 Sources and Pathways for Entering the Aquatic Environment

Plant and animal materials contribute organic carbon to the aquatic environment. Organic carbon compounds may be formed by photosynthesis within the aquatic environment. Runoff from agricultural lands and municipal and industrial waste discharges, especially from pulp and paper and meat processing plants, may further increase the levels of total organic carbon in water (McNeely *et al.* 1979).

6.3.9.3 Environmental Concentrations

Concentrations of organic carbon in surface waters range from nondetectable in newly risen rivers supplied by limestone springs to more than 100 mg·L^{-1} in bog and swamp waters (Sanborn *et al.* 1976). The total organic carbon content of natural waters may range from 1 to 30 mg·L^{-1} (McNeely *et al.* 1979). Environmental concentration ranges for organic carbon in Canadian surface waters are presented in Table 6-106. Environmental concentration ranges for lignin and tannin, two principal components of organic carbon, appear in Table 6-107.

Organic carbon concentrations in groundwater are generally lower than those in surface waters (Thurman 1985). However, there are exceptions. A NAQUADAT station in Newfoundland had a concentration of 1250 mg·L^{-1} (detection limit 0.5 mg·L^{-1} (total)) of organic carbon in a groundwater well sampled in 1981 (NAQUADAT 1985).

Dissolved organic carbon concentrations vary with the type of water from approximately 0.5 mg·L^{-1} for groundwater and seawater to more than 30 mg·L^{-1} for coloured water from swamps. Some pristine streams have low concentrations of dissolved organic carbon ranging from 1 to 3 mg·L^{-1}. Rivers and lakes contain more dissolved organic carbon, with concentrations ranging from 2 to 10 mg·L^{-1}. Swamps, marshes and bogs have concentrations of dissolved organic carbon ranging from 10 to 60 mg·L^{-1} (Thurman 1985).

Amounts of particulate organic matter also vary with the type of natural water. Groundwater and interstitial waters contain little or no particulate organic matter. Seawater contains only 0.01-0.1 mg·L^{-1} particulate organic matter, which consists mainly of algal detritus. Algal matter also constitutes the majority of particulate organic matter in lakes, which ranges in concentration from 0.1 to 1.0 mg·L^{-1} (Thurman 1985).

Particulate organic carbon is commonly about one-half the concentration of dissolved organic carbon in large rivers, and may equal dissolved organic carbon concentrations in the largest rivers and during periods of high discharge (Thurman 1985).

6.3.9.4 Forms and Fate in the Aquatic Environment

In water, organic carbon is principally composed of humic substances and partly degraded plant and animal materials that typically resist microbial degradation. Both tannin and lignin are constituents of many aquatic systems. Although they are not well-defined chemically, they are both polyphenols that have some carbohydrate character (Christman and Gjessing 1983). Lignin is one of the principal constituents of the woody structure of higher plants; it usually accounts for 15-30% of the dry weight of plant material. Tannin is a poorly characterized complex polyphenol (Health and Welfare Canada 1980). Photosynthetic activities also contribute dissolved organic carbon to aquatic systems. The amount of organic carbon components varies with discharge and especially with the growth cycles of vegetation (McNeely *et al.* 1979).

Table 6-106. Environmental Concentration Ranges for Organic Carbon in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.01-26	235	1980-1985
Western	ND^{1,2}-1610	15 658	Prior to 1980
Central	0.4^{1}-27	327	1980-1985
Atlantic	0.01-183	2 864	1980-1985

[1] Detection limit is 0.5 mg·L^{-1} (total).

[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-107. Environmental Concentration Ranges for Tannin and Lignin in Canadian Surface Waters

Region	Concentration range[1] (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	0.04-4.2	683	Prior to 1980
Western	0.1-2	64	Prior to 1980
Central	0-25.5	604	Prior to 1980
Atlantic	0.02-1	21	Prior to 1980

[1] Detection limit is 0.02 mg·L^{-1}.

Source: NAQUADAT 1985.

Humic substances are major constituents of both aquatic and terrestrial systems; most of the humates found in water result from leaching, although some are also produced by aquatic microorganisms. Humic substances may be described as coloured, predominantly aromatic, chemically complex, high-molecular-weight polyelectrolytes (Christman and Gjessing 1983).

The most common and stable high-molecular-weight humic substances in natural waters are humic and fulvic acids. The more soluble fulvic acid is found mainly in water, whereas humic acids are enriched in soils and sediment (Leenheer 1984).

Molecular weights of humic substances isolated from water range from 100 to 30 000. Humic substances are classified into three main fractions based on their solubilities: fulvic acid, which is soluble in both acid and alkali; humic acid, which dissolves in alkaline media, but is precipitated by acids; and humin, which is insoluble at all pH levels. Humic acid possesses an appreciable adsorptive capacity, and has the ability to form stable water-soluble and insoluble salts and complexes with both organic and inorganic compounds. The mechanisms of complex formation appear to be mainly hydrogen bonding and ion exchange, although other mechanisms, such as physical adsorption (Van der Waals forces and hydrophobic bonding), charge transfer, ligand exchange and chemisorption, cannot be ruled out (Christman and Gjessing 1983).

Most metals complex with humic substances in water. Complex formation can dramatically alter the solubility of metals; for example, soluble, naturally occurring humic substances in water may render iron up to 10^9 times more soluble in its complexed state, at pH 7, than its known solubility in the absence of complexing agents (Shapiro 1964). The ability of a number of natural waters in Ontario to complex copper has been demonstrated, with complexing capacities of up to 2.35 µmol·L^{-1} (0.149 mg·L^{-1}) reported (Shapiro 1964). The stability of metal-humate complexes increases with increasing pH, and decreases with increasing ionic strength of the medium. At low pH, and in order of decreasing stability of their complexes with fulvic acid in aqueous solution, the best known complexes are those of iron(III); aluminum(III); copper(II); nickel(II); cobalt(II); lead(II); calcium(II); zinc(II); cadmium(II); iron(II); manganese(II); and magnesium(II) (Shapiro 1964).

Under certain conditions, insoluble complexes with humic substances are formed. This phenomenon is exploited in the production of potable waters from coloured surface waters. Aluminum and iron appear to be capable of forming insoluble bridged complexes between the trivalent metal ion and two or more fulvic acid molecules (Stumm and Morgan 1962).

6.3.9.5 References

Christman, R.F. and E.T. Gjessing (eds.). 1983. Aquatic and Terrestrial Humic Materials. Ann Arbor Science Publ., Ann Arbor, Michigan. 538 pp.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

Health and Welfare Canada. 1980. Total organic carbon (TOC). *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 613-632.

Leenheer, J.A. 1984. Concentration, partitioning and isolation techniques. *In* Water Analysis. Vol. III. Organic Substances. R.A. Minear and L.K. Keith (eds.). Academic Press, Orlando, Florida. pp. 83-166.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Carbon – total organic carbon. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 10-11.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

Sanborn, J.R., R.L. Metcalf, W.N. Bruce and P.-Y. Lu. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5: 533-538.

Shapiro, J. 1964. Effect of yellow organic acids on iron and other metals in water. J. Am. Water Works Assoc. 56: 1062-1082.

Stumm, W. and J.J. Morgan. 1962. Chemical aspects of coagulation. J. Am. Water Works Assoc. 54: 971-992.

Thurman, E.M. 1985. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr. W. Junk Publ., Dordrecht, The Netherlands. 497 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.3.10 Organotin Compounds

6.3.10.1 Uses and Production

The two major uses of organotin compounds are in the production of plastics and as biocidal wood preservatives. Table 6-108 shows the organotin compounds having the highest consumption in Canada.

In Canada, the major end uses of organotin compounds are estimated as PVC stabilizers (80-82%), catalysts (16-17%), and biocides (2-3%). Dibutyltin bis(isooctyl mercaptoacetate) accounts for more than 75% by weight of the consumption of organotin compounds in Canada (Jones and Millson 1982). The total Canadian market (production and importation) of organotin compounds is estimated at more than 1000 $t \cdot a^{-1}$ (Jones and Millson 1982). It is not known what percentage of the total production and importation of organotin compounds is used as antifouling agents in marine paints in Canada (Jones 1985). Of the 10 organotin compounds consumed in large amounts (Table 6-108), only dibutyltin dilaurate and stannous 2-ethylhexoate are manufactured in Canada (MAR-TEC Ltd. 1979); these two compounds constitute less than 10% of the organotin compounds used in Canada (Thompson *et al.* 1985).

Table 6-108. Organotin Compounds Used in Canada

Compounds	Use
Dibutyltin bis-(isooctyl mercaptoacetate)	Stabilizer for poly(vinyl chloride) (PVC) used in siding, eavestroughs and soffits
Dibutyltin dilauryl mercaptide	Polyurethane foam catalyst; feed additive
Stannous 2-ethylhexanoate[1] (m)[2]	Polyurethane foam catalyst
Dibutyltin oxide	Precursor for dibutyltin dilaurate
Dibutyltin dilaurate (m)	Chicken feed additive; catalyst for urethanes; esterification catalyst
Tributyltin oxide (TBTO)	Slimicide in cooling water towers; antifouling additive for marine paint; wood preservative
Tributyltin fluoride (TBTF)	Antifouling additive for marine paint
Dioctyltin maleate	Stabilizer for rigid PVC pipe for potable water supplies
Dibutyltin diacetate	Catalyst for flexible foams
Dioctyltin bis-(isooctyl mercaptoacetate)	Stabilizer for plastics used in food packaging

[1] Not a true organotin but rather a tin salt.
[2] Manufactured in Canada.

Source: Jones and Millson 1982.

In 1981 and 1982, tributyltin oxide imports were 30 and 12 t, respectively. Imports of organotin compounds, except tributyltin oxide, in 1981, 1982 and 1983 were reported as 296, 287 and 997 t, respectively (Statistics Canada 1983, 1984).

6.3.10.2 Sources and Pathways for Entering the Aquatic Environment

The release of organotin compounds into the aquatic environment is, in general, through direct input via air or water as a result of production, processing, use or disposal, and indirectly through biotic and abiotic transformations (Thompson *et al.* 1985; Evans and Karpel 1985).

Only one manufacturing location for organotin compounds is known to exist in Canada; it converts dibutyltin oxide to dibutyltin dilaurate. Information on losses to the environment is unavailable. Facilities producing polyurethane or PVC resins stabilized with organotin compounds may release them into air, water or solid industrial wastes, but, again, quantities are unknown (Jones and Millson 1982; Thompson *et al.* 1985). In the United States, it has been estimated that 0.5% of production (0.054×10^6 kg) is lost to the environment by disposal routes at the manufacturing source and subsequent leaching (Zuckerman *et al.* 1978).

The greatest potential for direct contact with the aquatic environment is from biocidal applications, such as biocidal paints and preservatives (Thompson *et al.* 1985). The occurrence of high concentrations of butyltin species in harbours has been attributed to the use of biocidal paints (Maguire *et al.* 1982; Maguire 1984). It was estimated that 59 t of organotin compounds were released to the environment by antifouling coatings on U.S. marine craft over the 3-year lifetime of the coating (Lapp 1976).

Organotin compounds used in crop protection may also enter the environment during use. However, no data are available to determine input to the aquatic environment (Thompson *et al.* 1985).

No information is available on concentrations of organotin compounds in sanitary landfills or incineration effluents in Canada. In the United States, landfill and incineration are used to dispose of an estimated 2.3×10^6 kg of organotin compounds in PVC annually, whereas approximately 0.45×10^6 kg of organotin compounds in biocides are released each year to the environment via municipal sewers, surface waterways, harbours and oceans (U.S. EPA 1977). Leaching of organotin compounds from biocidal products and landfills also contributes to their presence in the aquatic environment (Jones and Millson 1982). The amounts released via these routes are unknown.

Atmospheric transport could explain the presence of methyltin species in areas remote from industrial activity (Maguire *et al.* 1982). Another possible source of organotin compounds is the methylation of inorganic tin (Thompson *et al.* 1985).

6.3.10.3 Environmental Concentrations

Most of the data available on organotin compounds are for Canadian waters and are presented in Table 6-109. International data are included for comparison.

6.3.10.4 Forms and Fate in the Aquatic Environment

Organotin compounds usually contain tin in the +4 oxidation state plus one to four aliphatic or aromatic groups directly bonded through carbon to tin. Organotin compounds may be represented by the formula R_nSnX_{4-n} ($n = 1\text{-}4$; R = alkyl or aryl; X = H,OR or halogen). In commercially significant mono-, di- and triorganotin compounds, the valency requirements of the tin are completed through bonding to halogen, sulphur or oxygen atoms. The oxygen or sulphur may form part of larger anionic organic groups (Jones and Millson 1982).

Very little information is available on the forms and fate of organotin compounds in the aquatic environment. In general, studies on the persistence of the major classes of organotin compounds indicate that abiotic and biotic degradation generally can occur via mechanisms of sequential dealkylation and dearylation. Sorption by soils and sediments also occurs; however, subsequent remobilization by biota is possible (Thompson *et al.* 1985). The primary mechanisms controlling the persistence of tri-*n*-butyltin compounds in aquatic ecosystems are photolysis in water and biological degradation in water and sediment. At temperatures and sunlight intensities prevalent in Canada, half-lives of at least several months are expected (Maguire and Tkacz 1985).

Methyltin compounds may be sequentially demethylated to inorganic tin. Photolytic half-lives of 30, 300 and 1500 h have been estimated for tri-, di- and monomethyltin, respectively (Blunden 1983). Tributyltin compounds do not dealkylate in the dark, nor do they volatilize (Maguire *et al.* 1983). There is some evidence for sorption to soils and sediments (Sheldon 1978) and for microbial dealkylation (Barug and Vonk 1980; Maguire *et al.* 1985). The tributyltin species (Bu_3Sn^+) was found to be fairly strongly bound to sterile Toronto Harbour sediment (partition coefficient of $\sim 10^3$). A half-life for tributyltin species as a result of desorption at 20°C was at least 10 months (Maguire and Tkacz 1985). Depending upon experimental conditions, photolytic half-lives for tributyltin compounds have been reported to be 18 d (Slesinger and Dressler 1978) and >89 d (Maguire *et al.* 1983). Photolytic half-lives for di- and monobutyltin compounds are considered to be similar. Tricyclohexyltin compounds are slowly volatilized, and there is some evidence to suggest that sorption by soil and sediment occurs (Blair 1975). Although no rate information is available, cyclohexyltin compounds photolytically degrade, releasing cyclohexane and cyclohexanol (Smith *et al.* 1976). Triphenyltin compounds are strongly bound to soil (Barnes *et al.* 1973) and undergo sequential dearylation in sunlight with a half-life of 14-21 d (Soderquist and Crosby 1978). Triphenyltin compounds may be slowly degraded by soil microorganisms (Barnes *et al.* 1973).

Methylation and demethylation of organotin compounds are likely to occur in the aquatic environment via both abiotic and biotic mechanisms. However, the environmental significance of these processes has not yet been elucidated (Thompson *et al.* 1985). The tributyltin species (Bu_3Sn^+) was degraded by sequential debutylation at 20°C in Toronto Harbour water and water-sediment mixtures, with half-lives of 5 and 4 months, respectively (Maguire and Tkacz 1985). A study of the degradation of tributyltin by bacteria from Toronto Harbour sediment revealed that at 20°C the degradation was twice as fast under anaerobic conditions than under aerobic conditions (Maguire *et al.* 1985).

Some organotin compounds may be accumulated by aquatic organisms. Calculated octanol/water partition coefficients (log P_{ow} <1-4.3) suggest that the potential for bioaccumulation of triorganotin compounds does exist, particularly for those compounds containing organic groups at least as large as the butyl group. Calculated bioconcentration factors range from <1 to 10^4, and are in general agreement with those observed in the limited field studies available (Thompson *et al.* 1985).

6.3.10.5 References

Barnes, R.D., A.T. Bull and R.C. Poller. 1973. Studies on the persistence of the organotin fungicide fentin acetate (triphenyltin acetate) in the soil and on surfaces exposed to light. Pestic. Sci. 4: 305-317. (Cited in Thompson *et al.* 1985.)

Barug, D. and J.W. Vonk. 1980. Studies on the degradation of bis(tributyltin) oxide in soil. Pestic. Sci. 11: 77-82. (Cited in Thompson *et al.* 1985.)

Blair, E.H. 1975. Biodegradation of tricyclohexyltin hydroxide. Environ. Qual. Saf. Suppl. 3: 406-409. (Cited in Thompson *et al.* 1985.)

Blunden, S.J. 1983. The ultraviolet degradation of the methyltin chlorides in carbon tetrachloride and water. J. Organomet. Chem. 248: 149-160. (Cited in Thompson *et al.* 1985.)

Table 6-109. Concentrations of Organotin Compounds in Fresh Water, Sediment and Fish

Species	Medium	Concentration ($\mu g \cdot L^{-1}$ Sn or $mg \cdot kg^{-1}$ Sn)	Location	Reference
Total Sn	Fresh water	0.004	General	Iverson and Brinckman 1978
Inorganic Sn	Fresh water	ND[1]-50.1	Canada	Maguire *et al*. 1982, 1986; Maguire and Tkacz 1985
		0.08-0.49	Lake Michigan	Hodge *et al*. 1979
	Freshwater surface microlayer	ND[2]	Canada	Maguire *et al*. 1982
	Sediment	ND[3]-15.5	Canada	Maguire 1984; Maguire and Tkacz 1985; Maguire *et al*. 1986
	Fish	ND[2]-0.90	Canada	Maguire *et al*. 1986
$MeSn^{3+}$	Fresh water	ND[1]-1.22	Canada	Maguire *et al*. 1982, 1986
		0.003-0.01	Lake Michigan	Hodge *et al*. 1979
	Sediment	ND[3]-17.19	Canada	Maguire *et al*. 1986
		ND[4]-0.88	Canada	Maguire *et al*. 1986
Me_2Sn^{3+}	Fresh water	ND[5]-0.034	Lake Michigan	Hodge *et al*. 1979
		ND[1]-0.40	Canada	Hodge *et al*. 1979; Maguire *et al*. 1986
	Sediment	ND[3]-0.17	Canada	Maguire *et al*. 1986
	Fish	ND[4]-0.18	Canada	Maguire *et al*. 1986
$MeSn^{3+}$	Fresh water	ND[6]-0.002	Rivers in southeastern U.S.A.	Byrd and Andreae 1982
		ND-0.18	Canada	Maguire *et al*. 1982, 1986
	Sediment	ND[3]-0.75	Canada	Maguire *et al*. 1986
$BuSn^{3+}$	Fresh water	0.009-0.51	Lake Michigan	Hodge *et al*. 1979
		ND[1]-8.48	Canada	Maguire *et al*. 1982, 1986; Maguire and Tkacz 1985
	Sediment	ND[3]-4.73	Canada	Maguire 1984; Maguire and Tkacz 1985; Maguire *et al*. 1986
Bu_2Sn^{2+}	Fresh water	0.004-0.62	Lake Michigan	Hodge *et al*. 1979
		ND[1]-7.30	Canada	Maguire *et al*. 1982, 1986; Maguire and Tkacz 1985
	Freshwater surface microlayer	ND[2]-2600	Canada	Maguire *et al*. 1982, 1986; Maguire and Tkacz 1985
	Sediment	ND[3]-8.51	Canada	Maguire 1984; Maguire and Tkacz 1985; Maguire *et al*. 1986
Bu_3Sn^{+}	Fresh water	ND[1]-2.91	Canada	Maguire *et al*. 1982, 1986; Maguire and Tkacz 1985
	Freshwater surface microlayer	ND[2]-60.7	Canada	Maguire *et al*. 1982
	Sediment	ND[3]-10.78	Canada	Maguire 1984; Maguire and Tkacz 1985; Maguire *et al*. 1986
	Fish	ND[4]-0.02	Canada	Maguire *et al*. 1986

[1] Quantitation limit is 0.01 $\mu g \cdot L^{-1}$ Sn.
[2] Quantitation limit is 0.50 $\mu g \cdot L^{-1}$ Sn.
[3] Quantitation limit is 0.01 $mg \cdot kg^{-1}$ Sn (dry weight).
[4] Quantitation limit is 0.01 $mg \cdot kg^{-1}$ Sn (wet weight).
[5] Detection limit is 0.0004 $\mu g \cdot L^{-1}$ Sn.
[6] Detection limit is 0.0001 $\mu g \cdot L^{-1}$ Sn.

Byrd, J.T. and M.O. Andreae. 1982. Tin and methyltin species in seawater: concentrations and fluxes. Science 218: 565-569. (Cited in Thompson *et al*. 1985.)

Evans, C.J. and S. Karpel. 1985. Organotin Compounds in Modern Technology. Elsevier Sci. Publ., Amsterdam, The Netherlands. 279 pp.

Hodge, V.F., S.L. Seidel and E.D. Goldberg. 1979. Determination of tin(IV) and organotin compounds in natural waters, coastal sediments and macro algae by atomic absorption spectrometry. Anal. Chem. 51: 1256-1259. (Cited in Thompson *et al*. 1985.)

Iverson, W.P. and F.E. Brinckman. 1978. Microbial metabolism of heavy metals. *In* Water Pollution Microbiology. Vol. 2. R. Mitchell (ed.). John Wiley & Sons, New York. pp. 201-232. (Cited in Thompson *et al*. 1985.)

Jones, P.A. 1985. Personal communication. Environmental Protection Service, Environment Canada, Ottawa.

Jones, P.A. and M.F. Millson. 1982. Organotins in the Canadian Environment: A Synopsis. Environmental Protection Service, Environment Canada, Ottawa. Economic and Technical Review Report EPS-3-EC-82-1.

Lapp, T.W. 1976. Study on Chemical Substances from Information Concerning the Manufacture, Distribution, Use, Disposal, Alternatives, and Magnitude of Exposure to the Environment and Man. Task II – The Manufacture and Use of Selected Alkyltin Compounds. Office of Toxic Substances, U.S. Environmental Protection Agency. EPA 560/6-76-011, PB-251819. 122 pp.

Maguire, R.J. 1984. Butyltin compounds and inorganic tin in sediments in Ontario. Environ. Sci. Technol. 18: 291-294.

Maguire, R.J. and R.J. Tkacz. 1985. Degradation of the tri-*n*-butyltin species in water and sediment from Toronto harbor. J. Agric. Food Chem. 33: 947-953.

Maguire, R.J., Y.K. Chau, G.A. Bengert, E.J. Hale, P.T.S. Wong and O. Kramer. 1982. Occurrence of organotin compounds in Ontario lakes and rivers. Environ. Sci. Technol. 16: 698-702.

Maguire, R.J., J.H. Carey and E.J. Hale. 1983. Degradation of tri-*n*-butyltin species in water. J. Agric. Food Chem. 31: 1060-1065. (Cited in Thompson *et al*. 1985.)

Maguire, R.J., D.L.S. Liu, K. Thomson and R.J. Tkacz. 1985. Bacterial degradation of tributyl tin. National Water Research Institute Report 85-82.

Maguire, R.J., R.J. Tkacz, Y.K. Chau, G.A. Bengert and P.T.S. Wong. 1986. Occurrence of organotin compounds in water and sediment in Canada. Chemosphere (in press).

MARTEC Ltd. 1979. Canadian Use Pattern Survey of Organotins, Phthalate Esters and Triaryl Phosphates. Document prepared for Environmental Protection Service, Environment Canada, Ottawa. (Cited in Thompson *et al.* 1985.)

Sheldon, A.W. 1978. Dissipation and detoxification of organotins in the environment. Proc. Annu. Mar. Coat. Conf. 18: IX-1 to IX-18. (Cited in Thompson *et al.* 1985.)

Slesinger, A.E. and I. Dressler. 1978. The environmental chemistry of three organotin chemicals. *In* Report of the Organotin Workshop. M. Good (ed.). Univ. of New Orleans, New Orleans, Louisiana, Feb. 17-19. pp. 115-162. (Cited in Thompson *et al.* 1985.)

Smith, G.N., F.S. Fischer and R.J. Axelson. 1976. Volatilization and photodecomposition of Plictran miticide. J. Agric. Food Chem. 24: 1225-1229. (Cited in Thompson *et al.* 1985.)

Soderquist, C.J. and D.G. Crosby. 1978. Determination of triphenyltin hydroxide and its degradation products in water. Anal. Chem. 50: 1435-1439. (Cited in Thompson *et al.* 1985.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Thompson, J.A.J., M.G. Sheffer, R.C. Pierce, Y.K. Chau, J.J. Cooney, W.R. Cullen and R.J. Maguire. 1985. Organotin Compounds in the Aquatic Environment: Scientific Criteria for Assessing their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 22494. 284 pp.

U.S. EPA. 1977. Assessment of the Need for, the Character of, and the Impact Resulting from Limitations on Selected Organotins. Phase I. Assessment of the Need for Limitations on Organotins. R.R. Wilkinson and I.C. Smith (eds.). Office of Toxic Substances, U.S. Environmental Protection Agency.

Zuckerman, J.J., R.P. Reisdorf, H.V. Ellis, III and R.R. Wilkinson. 1978. Organotins in biology and the environment. *In* Organometals and Organometalloids, Occurrence and Fate in the Environment. F.E. Brinckman and J.M. Bellama (eds.). Am. Chem. Soc. Symp. Ser. No. 82. pp. 388-424. (Cited in Thompson *et al.* 1985.)

6.3.11 Oil and Grease

Oil and grease are not definitive chemical substances, but may include thousands of organic chemicals with different physical, chemical and toxicological properties. They may be volatile or nonvolatile, soluble or insoluble, persistent or readily biodegradable (U.S. EPA 1976). Unlike other constituents that represent distinct chemical species, oil and grease are defined by the specific method used for their determination. In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Instead, groups of substances possessing similar physical characteristics are determined on the basis of their common solubility in trichlorotrifluoroethane. Other compounds, such as sulphur compounds, certain organic dyes and chlorophyll, may also be measured in this test (Greenberg *et al.* 1983).

Environmental concentration ranges for oil and grease in Canadian surface waters are presented in Table 6-110.

Table 6-110. Environmental Concentration Ranges for Oil and Grease in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<1	17	Prior to 1980
Western	<1-4	220	1980-1981
Central	0-2.9	127	Prior to 1980

[1] Detection limit is 1 $mg \cdot L^{-1}$.

Source: NAQUADAT 1985.

6.3.11.1 References

Greenberg, A.E., J.J. Connors and D. Jenkins. 1983. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

U.S. EPA. 1976. Quality Criteria for Water. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76/023. pp. 111-112.

6.3.12 Pesticides

6.3.12.1 Aromatic Carboxylic Acids

6.3.12.1.1 Dicamba

6.3.12.1.1.1 Uses and Production

Dicamba is a postemergence herbicide registered for use in Canada for the control of a variety of broadleaf weeds, including dandelions, chickweed and poison ivy, on lawns and noncroplands (e.g. around cottages). Commercial use of dicamba includes the control of primarily broadleaf weeds on croplands and on pasture/rangelands or turf. Application rates ranging from 0.1 to 11 $kg\text{-}ai \cdot ha^{-1}$ (ai = active ingredient) have been reported (Worthing 1983). Higher application rates are required to control brush and tree growth on rangeland and noncroplands such as rights-of-way. Fifteen companies are registered to market 30 products (11 domestic and 19 commercial) containing dicamba in Canada (Agriculture Canada 1985).

According to a 1982 survey of pesticides used in Quebec, dicamba was sold to farmers in the province. Although total amounts of all herbicides sold were reported, amounts for individual herbicides, such as dicamba, were not reported (Environment Canada/Ministère de l'Environnement du Québec 1984). In 1979, approximately 90% of land sown to cereal and oilseed crops in Saskatchewan received treatments with the herbicides dicamba, 2,4-D, triallate and trifluralin for weed control (Smith 1982). In 1981 and 1982, 473 and 1220 t, respectively, of formulated dicamba herbicide were imported into Canada. One tonne of technical-grade dicamba was imported in 1982, whereas no imports occurred in 1981 (Statistics Canada 1983). In Ontario, 45 130 kg were used on field crops, fruits and vegetables, and roadsides in 1983 (Ontario Ministry of Agriculture and Food 1984).

Additional names for dicamba that are used in Canada include Banvel D; Dycleer; Banvel Liquid Herbicide; Chipman Lawn Weedkiller K; Dyvel Liquid Herbicide; Green Cross Brushex Dicamba/2,4-D; Kil-Mor; and Killex Turf Herbicide (Agriculture Canada 1984; Environment Canada/Ministère de l'Environnement du Québec 1984).

6.3.12.1.1.2 Sources and Pathways for Entering the Aquatic Environment

Little information is available on the sources and pathways for entry of dicamba in the aquatic environment. The available studies suggest that small amounts of dicamba may reach adjacent waters during and shortly after application. Dicamba, applied at a rate of 1.1-2.2 kg-ai·ha^{-1} to clay loam soil (montmorillonite clay, pH 5-7, organic matter 1.5-2.0%) having a 3% slope, was found in surface runoff after a simulated rainfall of 1.3 cm·h^{-1}. Concentrations of 1.6 mg·L^{-1} were found 24 h after application, but decreased to 18 µg·L^{-1} after 4 months. The herbicide was not associated with suspended particulate matter in the runoff, but instead was dissolved in the runoff water. Although not measured, microbial degradation probably accounted for the reduced concentrations of dicamba after 4 months (Trichell *et al.* 1968). Dicamba concentrations as high as 0.7 µg·L^{-1} were found in lysimeter percolation water 10 months after application (5.6 kg-ai·ha^{-1}) to silt loam soil (1.72% organic matter, pH 5.0). Nearly 50% of the originally applied dicamba was, however, lost from soil 2 months after application. Residual concentrations of 0.23 and 0.54 µg·L^{-1} were found in surface runoff 3 and 4 months, respectively, after initial application. Residues in surface runoff were attributed to rain events (Glass and Edwards 1979). Residues in stream water draining a forested watershed increased significantly to a maximum concentration of 37 µg·L^{-1} in 5.2 h after the aerial application of dicamba at a rate of 1.2 kg-ai·ha^{-1}. Residues of dicamba in the stream water were attributed primarily to direct application to surface waters and spray drift. No residues were detected (detection limit 1 µg·L^{-1}) 11 d after initial application. Low concentrations (~2 µg·L^{-1}) of dicamba were observed in stream water after precipitation runoff events, and were attributable mainly to foliar washoff (Norris and Montgomery 1975). Dicamba was found (0.05-30 µg·L^{-1}) in the Thames River in southern Ontario in 1984, where it was regularly used for agriculture (Ralston 1986).

6.3.12.1.1.3 Environmental Concentrations

Only one sample result, taken prior to 1980, has been reported for dicamba in NAQUADAT (1985). It was reported in the Western region at a concentration below the detection limit of 0.01 µg·L^{-1}. Water samples collected from the LaSalle and Assiniboine rivers in Manitoba during 1983-84 contained dicamba in trace (<0.5 µg·L^{-1}) amounts (Williamson 1984).

6.3.12.1.1.4 Forms and Fate in the Aquatic Environment

Dicamba, 3,6-dichloro-2-methoxybenzoic acid (Figure 6-10), is a colourless solid melting at 114-116°C. It has a vapour pressure of 4.5 mPa at 25°C and a water solubility of 6.5 g·L^{-1} at 25°C (Worthing 1983).

In aqueous solution, dicamba is acidic (pK_a 1.90) (Carringer *et al.* 1975) and readily forms water-soluble salts with a variety of alkali metals and ammonium and amine ions. It is resistant to oxidation and hydrolysis under typical environmental conditions (Worthing 1983). In general, dicamba is considered to be nonpersistent in terrestrial and aquatic environments; information on its environmental dynamics in aquatic systems is, however, limited.

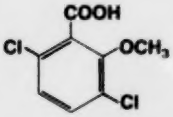


Figure 6-10. Dicamba.

Dicamba is considered to be mobile in the environment. It is not sorbed to any appreciable extent by particulate matter in soil-water suspensions. Very little adsorption of either the acid or the dimethylamine salt occurred in Canadian prairie soils composed of clay (6-69.5%), silt (10.4-33.2%), sand (5.3-81.6%) and organic matter (1.8-7.8%) with field moisture capacities of 10-41% and at pH 5.9-7.5 (Grover and Smith 1974). Soil distribution coefficients (K_d) in various Canadian soil types ranged from −0.14 to 0.30 (Grover 1977). In moist soils, dicamba and dicamba salts undergo dissociation with the resultant rapid elution of the dicamba anion, 3,6-dichloro-2-methoxybenzoate anion (Grover and Smith 1974). Dicamba, as the diethylamine salt, was not adsorbed onto organic matter at pH 5.5 and 24 ± 1°C. Some adsorption was, however, observed onto calcium-saturated montmorillonite clay suspensions at pH 6.0 (Carringer *et al.* 1975). Humic acid can sorb a small amount of dicamba from aqueous solution (~1%); prolonged washing of the humic acid – dicamba complex with distilled water failed to release any sorbed pesticide (Khan 1973). Although dicamba is not readily sorbed, its major biotic degradation product, 3,6-dichlorosalicylic acid, is sorbed by soil particulate matter (Baur *et al.* 1973).

Dicamba can volatilize from foliar and soil surfaces; the environmental significance of this process has, however, not been fully studied. Damage to sensitive crop species that has been attributed to vapour drift has been observed (Behrens and Lueschen 1979). No information is available on the evaporation of dicamba from surface waters. Pure dicamba, applied as a thin film and heated to 30°C, had a half-life of less than 7 d. The acid appeared to be more thermolabile than the salts (Baur *et al.* 1973). Although there was a 48% loss from bare planchets exposed to 35°C for 11 weeks, very little dicamba was lost over an 8-week period from sterile soils incubated at 35°C and various relative humidities (0-100%) (Burnside and Lavy 1966). In a field study in which dicamba was deposited on corn leaves, volatilization was observed up to 3 d after application (Behrens and Lueschen 1979).

Dicamba appears to be resistant to photodegradation. Pure dicamba irradiated at 365 nm did not degrade (Hahn *et al.* 1969). Likewise, in aqueous solution, the toxicity of dicamba to cucumber roots was not significantly reduced after exposure to sunlight for up to 16 h (Smith 1973).

Dicamba is considered to be nonpersistent in terrestrial systems (Smith 1982). It undergoes rapid degradation in moist, nonsterile soils. For example, 90% of the dicamba applied to Regina heavy clay (clay 70%, silt 25%, sand 5%, organic matter 4.2%, pH 7.5, field moisture capacity 40%) was lost after 5 weeks of incubation at 25°C, corresponding to a half-life of 2-3 weeks (Smith 1973). Less than 5% of the original dicamba remained in treated field plots containing sandy, loam soils (clay 10%, silt 25%, sand 65%, organic matter 4.6%, pH 7.6) 45 d after a summertime application (Smith and Muir 1984). Dicamba, sprayed on dykeland soil (clay 25%, silt 56%, sand 19%, organic matter 2.6%, pH 5.8) in Nova Scotia was rapidly lost, with only 5% remaining after 42 d (Stewart and Gaul 1977). In laboratory studies using aqueous soil suspensions held at 25°C, dicamba was rapidly lost under nonsterile conditions. Degradation was essentially complete after 3 weeks, with less than 1% remaining as the starting material after 9 weeks. The principal degradation product was 3,6-dichlorosalicylic acid, which further degraded with the release of carbon dioxide. No degradation was observed, however, in sterile soil suspensions after 9 weeks (Smith 1974).

Little information is available on the persistence of dicamba in water. Five hours after the aerial spraying of dicamba (1.12 kg-ai·ha^{-1}) in a forested area, residual concentrations up to a maximum of 37 μg·L^{-1} were found in stream water draining the watershed. Residue levels declined to background within approximately 3 d. The authors speculated that sorption to stream sediments or uptake by biota had occurred (Norris and Montgomery 1975). Dicamba applied at a rate of 4.3-4.5 kg·ha^{-1} to two small (0.11 and 0.2 ha) ponds in south-central Texas in June resulted in an initial water concentration of 11 mg·L^{-1}. The average loss was approximately 1.6 mg·L^{-1}·d^{-1}, with the most rapid loss occurring within the first 7 d of treatment. Dissipation was complete after approximately 40 d. The presence of aquatic vegetation or high turbidity apparently did not affect the rate of dicamba dissipation from the ponds. Dicamba was also rapidly dissipated when maintained in a nonsterile solution under continuous light in the laboratory (Scifres *et al.* 1973). The fate of dicamba in a model aquatic ecosystem containing water, sand and a series of food web organisms was also studied. Dicamba, initially applied to sorghum leaves in the terrestrial compartment, was leached into the water, and reached maximal concentrations in the water after 6 d. Dicamba persisted in water (10% loss after 32 d) in either conjugated or anionic form, and was slowly transformed to 5-hydroxydicamba. There was no evidence of biomagnification, as residue levels decreased with increasing trophic status (Yu *et al.* 1975).

6.3.12.1.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Pesticides Division, Registered Pest Control Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Pesticides Division, Registered Pest Control Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Baur, J.R., R.W. Bovey and H.G. McCall. 1973. Thermal and ultraviolet loss of herbicides. Arch. Environ. Contam. Toxicol. 1: 289-302.

Behrens, R. and W.E. Lueschen. 1979. Dicamba volatility. Weed Sci. 27: 486-493.

Burnside, O.C. and T.L. Lavy. 1966. Dissipation of dicamba. Weeds 14: 211-214.

Carringer, R.D., J.B. Weber and T.J. Monaco. 1975. Adsorption-desorption of selected pesticides by organic matter and montmorillonite. J. Agric. Food Chem. 23: 568-572.

Environment Canada/Ministère de l'Environnement du Québec. 1984. Les Pesticides en Agriculture au Québec en 1982. Service de la protection de l'environnement/Service de l'assainissement agricole, Montréal, Québec. 134 pp.

Glass, R.L. and W.M. Edwards. 1979. Dicamba in lysimeter runoff and percolation water. J. Agric. Food Chem. 27: 908-909.

Grover, R. 1977. Mobility of dicamba, picrolam, and 2,4-D in soil columns. Weed Sci. 25: 159-162.

Grover, R. and A.E. Smith. 1974. Adsorption studies with the acid and dimethylamine forms of 2,4-D and dicamba. Can. J. Soil Sci. 54: 179-186.

Hahn, R.R., O.C. Burnside and T.L. Lavy. 1969. Dissipation and phytotoxicity of dicamba. Weed Sci. 17: 3-8.

Khan, S.U. 1973. Interaction of humic acid with chlorinated phenoxyacetic and benzoic acids. Environ. Lett. 4: 141-148.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Norris, L.A. and M.L. Montgomery. 1975. Dicamba residues in streams after forest spraying. Bull. Environ. Contam. Toxicol. 13: 1-8.

Ontario Ministry of Agriculture and Food. 1984. Survey of pesticide use in Ontario 1983. Economics Information Report No. 84-05. 39 pp.

Ralston, J.G. 1986. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Scifres, C.J., T.J. Allen, C.L. Leinweber and K.H. Pearson. 1973. Dissipation and phytotoxicity of dicamba residues in water. J. Environ. Qual. 2: 306-309.

Smith, A.E. 1973. Transformation of dicamba in Regina heavy clay. J. Agric. Food Chem. 21: 708-710.

Smith, A.E. 1974. Breakdown of the herbicide dicamba and its degradation product 3,6-dichlorosalicylic acid in Prairie soils. J. Agric. Food Chem. 22: 601-605.

Smith, A.E. 1982. Herbicides and the soil environment in Canada. Can. J. Soil Sci. 62: 433-460.

Smith, A.E. and D.C.G. Muir. 1984. Determination of extractable and non-extractable radioactivity from small field plots 45 and 95 weeks after treatment with ^{14}C-dicamba, 2,4-dichloro-^{14}C-phenoxy acetic acid, ^{14}C-triallate and ^{14}C-trifluralin. J. Agric. Food Chem. 32: 588-593.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Stewart, D.K.R. and S.O. Gaul. 1977. Persistence of 2,4,-D, 2,4,5-T and dicamba in a dykeland soil. Bull. Environ. Contam. Toxicol. 18: 210-218.

Trichell, D.W., H.L. Morton and M.G. Merkle. 1968. Loss of herbicides in runoff waters. Weed Sci. 16: 447-449.

Williamson, D.A. 1984. A Preliminary Investigation into the Presence of Agricultural Pesticides in the LaSalle and Assiniboine Rivers, Manitoba, Canada. Environmental Management Services Branch, Manitoba Department of Environment and Workplace Safety and Health. Water Standards and Studies Report No. 84-5.

Worthing, C.R. 1983. The Pesticide Manual. A World Compendium. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 172.

Yu, C.-C., D.J. Hansen and G.M. Booth. 1975. Fate of dicamba in a model ecosystem. Bull. Environ. Contam. Toxicol. 13: 280-283.

6.3.12.2 Carbamate Pesticides

6.3.12.2.1 Uses and Production

Carbamate pesticides are synthetic relatives of the alkaloid physostigmine from *Physostigma venenosum* or calabar bean. Their activity is associated with considerable variation in structure, and individual compounds show a remarkable degree of insecticidal selectivity (low mammalian toxicity) and relatively rapid environmental degradability. For these reasons, broad-spectrum carbamate pesticides have replaced chlorinated hydrocarbons in many uses (Holmstedt 1972; NAS 1977).

Table 6-111. Carbamate Pesticides Registered for Use in Canada Under the Pest Control Products Act and Some Import Values

Pesticide[1]	Import quantity (t) 1981	Import quantity (t) 1982	Uses
Aldicarb (f)	—	—	Insecticide: beets, potatoes, tobacco and onions
Aminocarb (Matacil) (f)	9	9	Insecticide: crops, forests
Aminocarb (t)	104	206	For ultimate sale as formulated aminocarb
Asulam (f)	153	20	Herbicide: weeds
Bendiocarb (f)	—	—	Insecticide: ant baits
Benomyl (f)	—	—	Fungicide: seed dressing
Carbaryl (Sevin) (f)	250	137	Insecticide: flea collars, powders, crops; fungicide: crops
Carbaryl (t)	80	82	For ultimate sale as formulated carbaryl
Carbendazim-phosphate (f)	—	—	Fungicide
Carbofuran (f)	1288	915	Insecticide: crops; nematicide
Chlorpropham (f)	—	—	Herbicide: potato sprout inhibitor
Desmedipham (f)	—	—	Herbicide: postemergence
Dimetilan (f)	—	—	Insecticide: flypaper
Dioxacarb (f)	—	—	Insecticide: fly bait
Eptam (f)	239	728	Herbicide: selective pre-emergent
Ferbam (f)	2	—	Fungicide: fruit trees
Ferbam (t)	4	—	For ultimate sale as formulated Ferbam
Formetanate hydrochloride (f)	—	—	Miticide, insecticide, molluscicide: plants and trees
Mancozeb (f)	—	—	Fungicide: potatoes, seed protectant
Maneb (f)	432	477	Fungicide: seed treatment
Maneb (t)	18	—	For ultimate sale as formulated Maneb
Metam-sodium (f)	—	—	Fumigant
Methiocarb (f)	—	—	Molluscicide: slugs
Methomyl (f)	—	—	Insecticide: fly bait
Metiram (f)	—	—	Insecticide; fungicide: seed protectant
Nabam (f)	13	—	Miticide
Oxamyl (f)	—	—	Insecticide; nematicide
Phenmedipham (f)	26	63	Herbicide: postemergence
Pirimicarb (f)	9	10	Aphicide: selective
Potassium *n*-hydroxymethyl-*n*-methyldithiocarbamate (f)	—	—	Microbiocide
Potassium *n*-methyldithiocarbamate (f)	—	—	Microbiocide
Propham (f)	—	—	Herbicide: selective
Propoxur (Baygon) (f)	—	—	Insecticide: flies, fleas, wasps, ants
Sodium dimethyldithiocarbamate (f)	—	—	Microbiocide; slimicide
Triophanate-methyl (f)	—	—	Fungicide: potatoes, roses, firs, seed protectant
Thiram (f)	—	—	Fungicide; insecticide: animal pest repellant
Zineb (f)	53	103	Insecticide; fungicide: potatoes, tomatoes, vegetables
Ziram(f)	—	—	Microbiocide
Thiocarbamate base pesticides (unspecified formulations)	50	34	Herbicide; fungicides (predominantly)
Dithiocarbamate base pesticides (unspecified formulations)	595	717	Herbicides; fungicides (predominantly)
Carbamate base pesticides (unspecified formulations)	157	627	Insecticides (predominantly)

[1] f = formulated pesticide; t = technical grade.

Sources: Statistics Canada 1983; Agriculture Canada 1984.

The carbamate pesticides that are registered for use in Canada are listed in Table 6-111 with import values where applicable.

The most recent published information on amounts of carbamate pesticides sold in Canada was in 1977 (Table 6-112).

6.3.12.2.2 Sources and Pathways for Entering the Aquatic Environment

The major input of carbamates to the environment results from their application to forests and agricultural areas for pest control. Spray drift, runoff and leaching from treated terrestrial systems provide most of the input to the aquatic environment (Kuhr and Dorough 1976; Coady 1978). The effluents of carbamate pesticide production facilities may be significant point sources (Kuhr and Dorough 1976; McNeely *et al.* 1979).

6.3.12.2.3 Environmental Concentrations

Little information is available concerning environmental residues of carbamates (Kuhr and Dorough 1976; NAS 1977). This is expected, as existing evidence indicates that carbamates are not as persistent in the aquatic environment as organophosphate or organochlorine pesticides (Kuhr and Dorough 1976).

Aminocarb residues in a brook near a spray area (for spruce budworm) reached a peak concentration of 24 $\mu g \cdot L^{-1}$ within 3-4 h after application at a concentration of 70 $g \cdot ai \cdot ha^{-1}$ (ai = active ingredient). Concentrations of the compound decreased to nondetectable levels within 15-20 h of spray application. Only 2 of 26 fish sampled in this area had detectable tissue concentrations of 0.02 and 0.04 $mg \cdot kg^{-1}$, 2 d following the spraying (Coady 1978).

Table 6-112. Quantity of Carbamate Pesticides Sold in Canada in 1977

Carbamate pesticide	Quantity sold
Carbamate insecticides (without fungicides) (including carbaryl, carbofuran, bux, Baygon, lannate, Sevin, etc.)	3 187 189 kg
Carbamate herbicides (including Avadex, Avadex BW, CIPC, Eptam, IPC, Tillam, Vegadex and mixtures of carbamates)	4 485 656 kg
Thiram (a dithiocarbamate fungicide) (without insecticide)	9 579 L
Other dithiocarbamate fungicides (without insecticide) (including Maneb, Dithana M-45, Manzate D, Polyram, Ziram, etc.)	784 156 L

Source: Statistics Canada 1978.

Environmental concentration ranges for carbaryl and aldicarb in Atlantic region surface waters are presented in Table 6-113.

6.3.12.2.4 Forms and Fate in the Aquatic Environment

Carbamates comprise a diverse group of organic chemicals that are based on carbamic acid (H_2NCOOH). The acid does not exist in free form; the acid salts, however, are relatively stable. The alkyl and aryl esters of carbamic acid are relatively soluble in water and, in general, have low volatilities (Table 6-114). Under alkaline conditions, numerous carbamate compounds will hydrolyze (Kuhr and Dorough 1976; Verschueren 1983).

The environmental fates of carbamates vary widely; each compound's lifetime in a specific situation depends upon various physical and chemical parameters. Although some information is available on their persistence in terrestrial systems, relatively little information is available on their persistence in aqueous systems. In general, as a class, the carbamates are not considered to be long-term contaminants in the environment; they do not persist as long as many of the organochlorine pesticides under similar circumstances (Kuhr and Dorough 1976).

The major processes governing the fate of carbamates in the aquatic environment appear to be alkaline hydrolysis, photolysis and biodegradation, although rates of removal from the water column vary dramatically with the specific carbamate (Kuhr and Dorough 1976).

Alkaline hydrolysis of several carbamates has been demonstrated. The persistence of carbaryl, aminocarb and propoxur ($10\ \mu g \cdot L^{-1}$) was studied in raw surface water (pH 7.3-8.0) from the Little Miami River, a small river receiving domestic and industrial waste as well as agricultural runoff. All carbamates completely disappeared after 8 weeks. After 1 week, 5, 50 and 60% of the compounds carbaryl, propoxur and aminocarb, respectively, remained; however, after 4 weeks, carbaryl had completely disappeared, and only 10 and 30% of aminocarb and propoxur, respectively, remained (Eichelberger and Lichtenberg 1971). The persistence of carbaryl, propoxur, pyrolan and dimetilan (40 mg in 10 L of river water at pH 7.2 and 25°C) in Nile River (Egypt) water was examined. Carbaryl and propoxur completely disappeared after 1 week; however, the dimethyl carbamates remained unchanged for at least 3 months (Aly and El-Dib 1971). The hydrolytic half-lives at pH 9 and 27°C in distilled water of carbaryl, propham and chloropropham were found to be 0.15, $>10^4$ and $>10^4$ d, respectively. Alternatively, the hydrolytic half-lives of carbaryl at pH 5 and pH 7 were 1500 and 15 d, respectively. The hydrolytic half-lives of carbaryl in Hickory Hills pond water (pH 6.7) and USDA No. 1 pond water (pH 7.2) (both near Athens, Georgia) were 32 and 12 d, respectively (Wolfe *et al.* 1978). The rate of hydrolysis of carbofuran at 25°C also increases with increasing pH. At pH 5, the hydrolytic half-life was found to be more than 10^3 d, but decreased to 20 d at pH 7 and to less than 1 d at pH 8.5 (NRCC 1979). The fate of propoxur was studied in a lake water (25-cm depth) and sediment (5-cm depth) system consisting of an artificial pool held outdoors. At pH 7 and 27-36°C, the half-life for propoxur was less than 1 d. In small sealed glass vessels, at pH 7 and 5-22°C, the half-life was 2.3 d; in sterilized water in sealed containers, the half-life was 3.4 d (Flint and Shaw 1971).

Hydrolysis of carbamates is influenced by temperature. For example, a 1 C° increase in temperature is estimated to result in a 35% increase in the hydrolytic rate of carbofuran (FMC Corporation 1977).

Because carbamates have low vapour pressures, volatilization is not expected to be a significant process for their removal from the aquatic environment.

Direct and indirect photolysis studies have been conducted at wavelengths below 290 nm, and hence are not directly applicable to natural sunlight conditions (NRCC 1982a). The direct photolytic half-lives of carbaryl and propham in distilled water exposed to sunlight were 6.6 and 254 d, respectively. The rates of photolytic degradation did not vary with pH in the range of pH 5-9 (Wolfe *et al.* 1978). Carbofuran in distilled water at pH 7 degraded upon exposure to light at 300-400 nm with a half-life of approximately 5-6 d. However, in the presence of a photosensitizer, such as benzophenone, the half-life decreased to approximately 1.8 d (Palmere 1978). Indirect evidence suggests that propoxur may be relatively resistant to photodegradation at wavelengths above 285-290 nm, although degradation has been observed upon exposure to ultraviolet light. Propoxur is degraded only slowly in aqueous solution; however, degradation does occur more rapidly in the presence of photosensitizers (NRCC 1982a).

Sorption does not appear to play a significant role in removing carbamates from the water column. Because they are water-soluble (Table 6-114), it is expected that only a small fraction of the carbamates present in aqueous systems would be associated with sediments. Sediment concentrations of carbofuran are not expected to greatly exceed those in the water column (NRCC 1979). Propoxur is only weakly adsorbed by water-saturated soils (NRCC 1982a). Aldicarb leaching from clay loam and muck soils was limited; leaching from coarse sand was, however, extensive (Coppedge *et al.* 1977).

Several carbamates have been found to be readily biodegradable. Consecutive additions of carbaryl to Nile River water demonstrated that there was some type of acclimation of microbes to carbaryl. By the fourth addition, carbaryl, at a concentration of $17.5\ mg \cdot L^{-1}$, was almost completely degraded in approximately 1 d. In a 50:50 mixture of sewage and

Table 6-113. Environmental Concentration Ranges for Carbaryl and Aldicarb in the Atlantic Region Surface Waters of Canada

Carbamate pesticide	Region	Concentration range ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year
Carbaryl	Nova Scotia	<0.03-0.05[1]	47	1984
	Nova Scotia (1 station: lake)	0.10 and 2.00[1] (maximum upper limits)	2	1984
Aldicarb	New Brunswick	<0.02[2]	17	1983

[1] Detection limit is 0.04 $\mu g \cdot L^{-1}$.
[2] Detection limit is 0.09 $\mu g \cdot L^{-1}$.

Source: NAQUADAT 1985.

Table 6-114. Physical-chemical Properties of Some Carbamate Insecticides

Common names	Chemical name	Melting point (°C)	Vapour pressure (Pa (°C))	Water solubility ($mg \cdot L^{-1}$ (°C))
Aldicarb	2-methyl-2-(methylthio)propanol *o*-[(methylamino)carbonyl]oxime	98-100	1.3×10^{-2} (25)	0.6% (25)
Aminocarb (Matacil)	4-dimethylamino-*m*-tolyl methylcarbamate	93-94		
Asulam	methyl sulphanilylcarbamate	143-143		0.5%
Propoxur (Baygon)	2-isopropoxyphenyl methylcarbamate	91	8.7×10^{-3} (20)	0.1-0.2%
Carbaryl (Sevin)	1-naphthyl methylcarbamate	142	<10 (26)	40 (30)
Carbofuran	2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate	150-152	2.7×10^{-4} (33)	700 (25)
Eptam	*S*-ethyl dipropyl(thiocarbamate)		47 (25)	370
Nabam	disodium ethylene bis(dithiocarbamate)			20%
Propham	isopropyl carbanilate	86-88		250

Source: Verschueren 1983.

water, the degradation of carbaryl was even faster (Aly and El-Dib 1971). In another study, the biodegradation of carbaryl was found to be slower, with a half-life of more than 10^4 d, based on a bacterial concentration of 0.1 $mg \cdot L^{-1}$ (Wolfe *et al.* 1978). Propoxur may be rapidly degraded by certain microorganisms when cultured under aerobic conditions; half-lives of less than 1 d have been recorded (Gupta *et al.* 1975; NRCC 1982a). Microbial degradation of propham is expected to be relatively rapid, with a half-life of 3.2 d (Wolfe *et al.* 1978). Under field conditions, aldicarb was found to be degraded in soils, and had a half-life of approximately 7 d in loam soil (Coppedge *et al.* 1977).

Bioaccumulation of carbamates is not expected to be significant in the aquatic environment because of their generally weak lipophilic character and relatively rapid degradation. Bioconcentration factors in fish of 6 and 8.9 for carbofuran (NRCC 1979) and propoxur (Neely *et al.* 1974), respectively, have been reported. Aminocarb had half-lives of 1 d in rainbow trout (*Salmo gairdneri*) fry (Lockhart *et al.* 1984), 2 d in brown bullheads (*Ictalurus nebulosus*) (Richardson and Qadri 1982) and <10 d in channel catfish (*Ictalurus punctatus*) (Lamb and Roney 1976; NRCC 1982b). Carbofuran had a half-life of approximately 4 d in bluegill sunfish (*Lepomis macrochirus*) (NRCC 1979). In terrestrial-aquatic ecosystem studies, biomagnification of carbofuran was not demonstrated (Metcalf *et al.* 1971; Yu *et al.* 1974).

6.3.12.2.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Aly, O.M. and M.A. El-Dib. 1971. Studies of the persistence of some carbamate insecticides in the aquatic environment. I. Hydrolysis of Sevin, Baygon, pyrolan and dimetilan in waters. Water Res. 5: 1191-1205.

Coady, L.W. 1978. Immediate Chemical and Toxicological Influences of Aerially Applied Fenitrothion and Aminocarb in Selected Newfoundland Streams. Environmental Protection Service – Atlantic Region, Environment Canada, St. John's, Newfoundland. Surveillance Report EPS-5-AR-78-1.

Coppedge, J.R., D.L. Bull and R.L. Ridgway. 1977. Movement and persistence of aldicarb in certain soils. Arch. Environ. Contam. Toxicol. 5: 129-141.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Flint, D.R. and H.R. Shaw. 1971. The mobility and persistence of baygon in soil and water. Chemagro Corp., Missouri. Unpubl. Rep. No. 30589. (Cited in NRCC 1982a.)

FMC (Food Machinery Chemical) Corporation. 1977. Carbofuran environmental impact data. Unpublished report. (Cited in NRCC 1979.)

Gupta, K.G., R.K. Sud, P.K. Aggarwal and J.C. Aggarwal. 1975. Effect of baygon on some soil biological processes and its degradation by a *Pseudomonas* sp. Plant Soil 42: 317-325.

Holmstedt, B. 1972. The ordeal of Old Calabar: The pageant of *Physostigma venenosum* in medicine. *In* Plants in the Development of Modern Medicine. T. Swain (ed.). Harvard University Press, Cambridge, Massachusetts. (Cited in Kuhr and Dorough 1976.)

Kuhr, R.J. and H.W. Dorough. 1976. Carbamate Insecticides: Chemistry, Biochemistry, and Toxicology. CRC Press, Inc., Cleveland, Ohio. 301 pp.

Lamb, D.W. and D.J. Roney. 1976. Accumulation and persistence of residues in channel catfish exposed to Matacil[14]. Mobay Chem. Corp. Rep. 49309. Pittsburgh, Pennsylvania. (Cited in NRCC 1982b.)

Lockhart, W.L., D.A. Metner, B.N. Billeck, G.P. Rawn and D.C.G. Muir. 1984. Bioaccumulation of some forestry pesticides in fish and aquatic plants. *In* Chemical and Biological Controls in Forestry. W.Y. Garner and J. Harvey (eds.). Am. Chem. Soc. Symp. Ser. No. 238. pp. 298-315.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

Metcalf, R.L., G.K. Sangha and I.P. Kapoor. 1971. Model ecosystems for the condition of pesticide biodegradability and ecological magnification. Environ. Sci. Technol. 5: 709-713.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NRCC. 1979. Carbofuran: Criteria for Interpreting the Effects of its Use on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16740. 191 pp.

NRCC. 1982a. Effects of Propoxur on Environmental Quality with Particular Reference to its Use for Control of Biting Flies. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18572. 238 pp.

NRCC. 1982b. Aminocarb: the Effects of its Use on the Forest and the Human Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18979. 253 pp.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

Palmere, R.M. 1978. Photodecomposition of carbofuran. FMC (Food Machinery Chemical) Corporation Report P-0157. Unpublished report. (Cited in NRCC 1979.)

Richardson, G.M. and S.U. Qadri. 1982. Acute toxicity, kinetics and metabolism of aminocarb in the brown bullhead (*Ictalurus nebulosus*). Water Pollut. Res. Can. 17: 153-158.

Statistics Canada. 1978. Sales of Pest Control Products by Canadian Registrants 1977. Catalogue No. 46-212.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Wolfe, N.L., R.G. Zepp and D.F. Paris. 1978. Carbaryl, propham, and chloropropham: a comparison of the rates of hydrolysis and photolysis with the rate of biolysis. Water Res. 12: 565-571.

Yu, C.-C., G.M. Booth, D.J. Hansen and J.R. Larsen. 1974. Fate of carbofuran in a model ecosystem. J. Agric. Food Chem. 22: 431-434.

6.3.12.3 Chlorophenoxy Compounds

6.3.12.3.1 2,4-D

6.3.12.3.1.1 Uses and Production

2,4-dichlorophenoxyacetic acid, also known as 2,4-D, is registered in Canada as a herbicide (Agriculture Canada 1984). It is widely used as a systemic herbicide to control broadleaf weeds in cereal cropland and on industrial property, lawns, turf, pastures and noncropland (NRCC 1978; Weed Science Society of America 1979; Worthing 1983). Most dicotyledonous crops are susceptible to the herbicide at normal application rates (Weed Science Society of America 1979; Que Hee and Sutherland 1981). Other major uses of 2,4-D in Canada are for grain farming, where it boosts yields 10-15% by eliminating competing weeds; forestry, where it is used to suppress the growth of less desirable hardwoods; and weed control along, for example, rights-of-way. In lakes, ponds and ditches, 2,4-D is applied to kill rooted macrophytes as well as floating and submerged weeds. The various uses differ primarily in the quantities of herbicide applied and the mode and frequency of application required for control of unwanted plants (NRCC 1978).

2,4-D is produced commercially by the chlorination of phenol to form 2,4-dichlorophenol, followed by reaction with monochloroacetic acid to form 2,4-D. Commercial 2,4-D formulations are generally composed of the salts or esters (ethyl, isopropyl, butyl, amyl, heptyl, octyl) of the acid (U.S. EPA 1974). The esters are synthesized by the reaction of 2,4-D with the appropriate alcohols. Salts are made by the addition of the appropriate amine or inorganic hydroxide to the acid (NRCC 1978). Both 2,4-D esters and amines are used in the Prairie Provinces. In 1976, the 2,4-D formulations applied in Saskatchewan, Alberta and Manitoba contained about 27, 33 and 81% amine salt, respectively (Gummer 1979).

2,4-D was produced in Edmonton until 1983, when 4500 t were manufactured (CORPUS Information Services 1983).

Table 6-115 lists importation of 2,4-D, 2,4-D esters and 2,4-D amine formulations.

Additional names for 2,4-D include Agrotect, Amoxone, Aqua-Kleen, Chipco Turf Herbicide D, Chloroxone, Crop Rider, D50, Dacamine*, Ded-Weed, Dormone, Esteron*, Esterone, Fernesta, Fernamine, Fernoxone, Feroxone, Formula 40, Hedonal, Lawn-Keep, Macondray, Miracle, Pennamine D, Planotox, Plantgard, Salvo, Tributon, U46, Vergemaster, Verton 2D, Visko-Rhap Low Volatile 4L, Weedar*, Weedez, Weedone*, Weed-Rhap and Wonder Bar (McNeely *et al.* 1979). 2,4-D can be present as the acid, low-volatility esters, sodium salt and dimethylamine, diethanolamine or other amine salts (Agriculture Canada 1984).

Commercial formulations of 2,4-D have been found to contain polychlorinated dibenzo-*p*-dioxins (PCDDs) (NRCC 1981).

6.3.12.3.1.2 Sources and Pathways for Entering the Aquatic Environment

2,4-D enters the aquatic environment from such industries as herbicide manufacturing and packaging plants. Another source of 2,4-D input to the aquatic environment is municipal effluents. 2,4-D also drifts into the atmosphere during application, causing localized damage to sensitive crops, and is transported over long distances. 2,4-D is applied directly to lakes, ponds and ditches to control weeds. Agricultural runoff is a major contributor of 2,4-D to surface waters (NRCC 1978; Gummer 1979; Nagy and Painter 1985).

6.3.12.3.1.3 Environmental Concentrations

High concentrations of 2,4-D in water have occurred at sites below urban centres. For example, a concentration of 4.33 $\mu g \cdot L^{-1}$ was recorded in Wascana Creek below Regina, Saskatchewan, and 3.40 $\mu g \cdot L^{-1}$ was recorded in the Red River near Selkirk, Manitoba. The concentration of 2,4-D in the effluent from an industrial plant located a few kilometres east of Edmonton, Alberta, was found to be as high as 4.34 $mg \cdot L^{-1}$ (Gummer 1979).

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*Names registered for use in Canada (Agriculture Canada 1984).

Table 6-115. Importation of 2,4-D and its Ester and Amine Formulations into Canada

Compound	Amount (t) 1981	1982	1983
2,4-D (technical grade)	55	331	1533
2,4-D and 2,4-D ester (formulated herbicide)	764	2935	1017
2,4-D ester and amine formulations	1923	4625	2607

Sources: Statistics Canada 1983, 1984.

Surface water samples taken between 1971 and 1977 in western Canada had 2,4-D concentrations ranging from below the detection limit (4 $ng \cdot L^{-1}$) to 334 $ng \cdot L^{-1}$. Of the 1386 tests performed, excluding districts remote from agricultural influence, 69% had detectable 2,4-D levels (Gummer 1979). Results of a preliminary investigation into the presence of agricultural pesticides in the LaSalle River in Manitoba during 1983-1984 indicated the presence of 2,4-D in concentrations ranging from 11 to 130 $ng \cdot L^{-1}$ (Williamson 1984).

Results of the 1974 sampling of eight agricultural watersheds in Ontario for phenoxy herbicides showed that 2,4-D was present in 39% of the water samples, with a mean residue concentration of 0.2 $\mu g \cdot L^{-1}$ (range: <0.1-16 $\mu g \cdot L^{-1}$). The following year, 11 agricultural mini-watersheds were sampled for phenoxy herbicides. Of the 404 samples analyzed, 38 (9.4%) contained 2,4-D; 33 contained less than 1 $\mu g \cdot L^{-1}$; 2 contained 1-2 $\mu g \cdot L^{-1}$; 1 contained 16 $\mu g \cdot L^{-1}$; and 1 contained 320 $\mu g \cdot L^{-1}$ (Frank *et al.* 1978).

The highest loadings of 2,4-D were in the watershed of Hillman Creek, Ontario, where no agricultural uses were found, but where rights-of-way were treated. In most watersheds, the loss in runoff water was between 0.3 and 6.0 g per season per watershed. Only in Big Creek and Hillman Creek were there losses as high as 66.5 and 328 g. These latter losses appeared to be the result of applications that caused direct contamination of stream water. Losses occurred mainly in June and July, at the height of the spraying season (Frank *et al.* 1978).

Investigations of farm ponds and wells in Ontario for suspected phenoxy herbicide contamination indicated that 48% of the ponds and 60% of the wells had, in fact, been contaminated. Of the contaminated wells, 81% contained detectable 2,4-D concentrations. Ponds, where equipment was filled, cleared or emptied, contained 2,4-D in concentrations ranging from trace (<0.1 $\mu g \cdot L^{-1}$) to 1.5 $\mu g \cdot L^{-1}$. Pond residues, as a result of surface runoff, ranged in concentration from less than 0.1 to 4 $\mu g \cdot L^{-1}$ (Frank 1970-1974).

One study at Buckhorn Lake, Ontario, where 2,4-D is applied to control water weeds, reported two distinct peak concentrations of 4.4 $\mu g \cdot L^{-1}$ (late June) and 1.9 $\mu g \cdot L^{-1}$ (late August). The first peak was the result of direct application, and the second release of 2,4-D was probably from the decaying plants. The observed rates of disappearance of 2,4-D, however, indicated a limited persistence in the lake (Nagy and Painter 1985). In a 2-year study of the fate and effects of 2,4-D in experimental pond ecosystems, Nagy *et al.* (1985) calculated half-lives of 17 d for the first year and 35 d for the second. Increased pH, due to macrophyte growth, in the ponds during the second year of treatment resulted in the greater persistence of the 2,4-D.

Table 6-116. Environmental Concentration Ranges for 2,4-D in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<4-15	196	Prior to 1980
Western	4-700	1340	1980-1982
Central	<4-16	4	1980-1981
Atlantic	4-10	45	1980-1985
	30-620 (maximum upper limits)	8	1980, 1984

[1] Detection limit is <4 $ng \cdot L^{-1}$.

Source: NAQUADAT 1985.

NAQUADAT data on 2,4-D from the various regions of Canada are presented in Table 6-116.

6.3.12.3.1.4 Forms and Fate in the Aquatic Environment

Commercial 2,4-D formulations are generally composed of the salts or esters of the acid. 2,4-D itself is chemically stable, but its esters are rapidly hydrolyzed to the free acid (Que Hee and Sutherland 1981; Worthing 1983). The solubility of 2,4-D in water is 540 $mg \cdot L^{-1}$ at 20°C; its major breakdown product, 2,4-dichlorophenol, has a solubility of 4500 $mg \cdot L^{-1}$. The salts of 2,4-D are generally highly soluble, but the esters are much less soluble (NAS 1977). Facile hydrolysis occurs at 25°C in basic solutions; hydrolytic half-lives are less than 5 min (Smith 1972). Hydrolytic half-lives at 28°C and pH 6-9 vary between 4 and 50 d (Zepp *et al.* 1975). The carbonyl functional group of the acid readily ionizes ($pK_a \simeq 3$) in aqueous media to yield the anion (NRCC 1978). In terrestrial environments, hydrolysis occurs within 2-3 d at normal temperatures in moist soils (NRCC 1978).

Because 2,4-D has an ultraviolet absorption maximum in water in the 280- to 290-nm range, it will absorb some radiation, and can be photochemically degraded. Rapid degradation of 2,4-D occurs in aqueous solutions (50% disappearance in 50 min) at pH 7 in the presence of sunlight or ultraviolet radiation (Crosby and Tutass 1966). 2,4-D decomposes to 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzene triol and polymeric humic acids (NAS 1977).

Volatilization is not expected to be an important removal process of 2,4-D or its salts above pH 4. However, if hydrolysis of ester formulations is not rapid, some volatilization may occur from surface waters (NRCC 1978).

Because 2,4-D is predominantly anionic in form in the range of pH 4-9, its adsorption onto negatively charged surfaces in either terrestrial or aquatic environments would not be extensive. The adsorption of 2,4-D on clay particles has been shown to be pH-dependent, being nil or negative at basic or neutral pH, moderate at pH values near the pK_a and positive at low pH. It is believed that the relative properties of the anionic and molecular forms of 2,4-D determine the extent of adsorption at various pH values (NRCC 1978). 2,4-D may be readily adsorbed by muck soil and peat moss. A variety of other adsorbents have been studied; the relative strength of adsorption of 2,4,-D at an equilibrium concentration of 1 $mg \cdot L^{-1}$ decreased in the following order: activated charcoal > anion-exchange resin > peat moss > cellulose triacetate > wheat straw > cellulose powder > silica gel > cation-exchange resin > kaolinite > montmorillonite (Grover and Smith 1974). In a study of the application of 2,4-D, as ester and amine formulations, to freshwater ponds, it was found that suspended particulate matter had no significant effect on herbicide removal from the water column (Scott *et al.* 1981).

Microbial degradation of 2,4-D contributes to its rapid breakdown in water (U.S. EPA 1974). Aerobic conditions are required for significant microbial degradation; half-lives under such conditions can be short, in the order of 1 to several weeks. Under anaerobic conditions, the half-lives can exceed 80-120 d (NRCC 1978). 2,4-D also undergoes microbial degradation in soils; breakdown is favoured by moist, warm conditions and high organic content (Loos 1975).

A significant fraction of the total aquatic ecosystem load of 2,4-D has been observed to be entrained by plants (Soderquist and Crosby 1975) and phytoplankton (Wojtalik *et al.* 1971). Residues in aquatic plants and plankton have been observed to persist as long as 2-6 months (Wojtalik *et al.* 1971). Nagy *et al.* (1985) observed that 2,4-D was released back into the water column upon decomposition of Eurasian water milfoil (*Myriophyllum spicatum*). Bioconcentration factors for aquatic animals are usually quite low, and biomagnification along the aquatic web is not considered significant (NRCC 1978). Bioconcentration factors of 13, based on water solubility, and 0.8, based on soil adsorption coefficient, have been estimated (Kenaga 1980).

6.3.12.3.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

CORPUS Information Services. 1983. 2,4-Dichlorophenoxyacetic acid (includes dry 2,4-D acid, amines, esters). CPI Product Profile. Don Mills, Ontario.

Crosby, D.G. and H.O. Tutass. 1966. Photodecomposition of 2,4-dichlorophenoxyacetic acid. J. Agric. Food Chem. 14: 596-599.

Frank, R. 1970-1974. Annual Report – Analysis of Samples Connected with Herbicide Damage Investigations. Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food, Guelph, Ontario. (Cited in NRCC 1978.)

Frank, R., H.E. Braun, M. Holdrinet, G.J. Sirons and B.D. Ripley. 1978. Monitoring Stream Water for Pesticides in Eleven Agricultural Watersheds in Southern Ontario, Canada, 1974-1977 (Project 4). International Joint Commission Technical Report, Windsor, Ontario.

Grover, R. and A.E. Smith. 1974. Adsorption studies with the acid and diethylamine forms of 2,4-D and dicamba. Can. J. Soil Sci. 54: 179-186.

Gummer, W.D. 1979. Pesticide Monitoring in the Prairies of Western Canada. Water Quality Branch – Western and Northern Region, Inland Waters Directorate, Environment Canada, Regina, Saskatchewan. Water Quality Interpretive Rep. No. 4.

Kenaga, E.E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotoxicol. Environ. Saf. 4: 26-38.

Loos, M.A. 1975. Phenoxyalkanoic acids. Chap. 1. *In* Herbicides: Chemistry, Degradation, and Mode of Action. Vol. 1. 2nd edition. P.C. Kearney and D.D. Kaufman (eds.). Marcel Dekker, New York. pp. 1-128.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

Nagy, E. and D.S. Painter. 1985. Seasonal variations of 2,4-D in Buckhorn Lake. Water Pollut. Res. Can. 20: 106-117.

Nagy, E., D.S. Painter and B.F. Scott. 1985. Fate and impact of 2,4-D in a pond ecosystem. *In* Proc. 1st Int. Symp. on Watermilfoil (*Myriophyllum spicatum*) and Related Haloragaceae Species, July 23-24, 1985, Vancouver, British Columbia. pp. 202-214.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

NRCC. 1978. Phenoxy Herbicides – Their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16075. 440 pp.

NRCC. 1981. Polychlorinated Dibenzo-*p*-dioxins: Criteria for their Effects on Man and his Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18574. 251 pp.

Que Hee, S.S. and R.G. Sutherland. 1981. The Phenoxyalkanoic Herbicides. Vol. 1. Chemistry, Analysis and Environmental Pollution. CRC Press, Inc. Boca Raton, Florida. 321 pp.

Scott, B.F., D.S. Painter, E. Nagy, B.J. Dutka and W.D. Taylor. 1981. Fate and Effects of 2,4-D Formulations as Herbicides in Aquatic Ecosystems. Part 1. National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario. 73 pp.

Smith, A.E. 1972. The hydrolysis of 2,4-dichlorophenoxyacetate esters to 2,4-dichlorophenoxyacetic acid in Saskatchewan soils. Weed Res. 12: 364-372. (Cited in NRCC 1978.)

Soderquist, C.J. and D.G. Crosby. 1975. Dissipation of 4-chloro-4-methylphenoxyacetic acid (MCPA) in a rice field. Pestic. Sci. 6: 17-33.

Statistics Canada. 1983. Imports. Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-203.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1974. The Herbicide 2,4-D. Office of Pesticides Programs, U.S. Environmental Protection Agency, Washington, D.C. 207 pp.

Weed Science Society of America. 1979. Herbicide Handbook. 4th edition. Champaign, Illinois.

Williamson, D.A. 1984. A Preliminary Investigation into the Presence of Agricultural Pesticides in the LaSalle and Assiniboine Rivers, Manitoba, Canada. Environmental Management Services Branch, Manitoba Department of Environment and Workplace Safety and Health. Water Standards and Studies Report No. 84-5.

Wojtalik, T.A., T.F. Hall and L.O. Hill. 1971. Monitoring ecological conditions associated with wide-scale applications of DMA 2,4-D to aquatic environments. Pestic. Monit. J. 4: 184-203.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 153.

Zepp, R.G., N.L. Wolf, J.A. Gordon and G.L. Baughman. 1975. Dynamics of 2,4-D esters in surface waters: hydrolysis, photolysis, and vaporization. Environ. Sci. Technol. 9: 1144-1150.

6.3.12.3.2 2,4,5-T

6.3.12.3.2.1 Uses and Production

2,4,5-T is used alone or with 2,4-D for the control of unwanted shrubs and trees. It is applied as foliage, dormant shoot or basal bark spray. It is also used for girdling, injection or cut-stump treatment. 2,4,5-T is absorbed through roots, foliage and bark. Esters of low volatility are used for ultra-low-volume applications (Worthing 1983).

The latest available information indicates that 91.6 t of 2,4,5-T were sold in Canada in 1977 to make up a mixture containing

2,4-D and 2,4,5-T for use as herbicides (Statistics Canada 1978). 2,4,5-T was sold in Quebec in 1982, but the amount was not reported (Environment Canada/Ministère de l'Environnement du Québec 1984). No importation of 2,4,5-T has occurred in recent years (1981-1982) in Canada (Statistics Canada 1983).

Forms of 2,4,5-T that are used in Canada include 2,4,5-T present as dimethylamine salt, monoethanolamine salt, *n*-oleyl-1,3-propylenediamine salt, triethylamine salt and low-volatility esters (Agriculture Canada 1984). Additional names for 2,4,5-T include Chipman Brushkiller 600 LV EC Liquid and Co-op LV Brush Killer 400 (Environment Canada/Ministère de l'Environnement du Québec 1984).

Technical 2,4,5-T formulations have been found to contain polychlorinated dibenzo-*p*-dioxins, particularly 2,3,7,8-TCDD (see Section 6.3.14.3). Modern methods of manufacture of 2,4,5-T limit the amount of dioxin contaminants to less than 0.01 mg·kg^{-1} 2,4,5-T (Worthing 1983).

6.3.12.3.2.2 Sources and Pathways for Entering the Aquatic Environment

When sprayed as an aqueous emulsion or solution, 2,4,5-T may be lost to the atmosphere via spray drift and evaporation (NRCC 1978). 2,4,5-T has been identified in rainwater samples (Weibel *et al.* 1965) and in dust samples (Cohen and Pinkerton 1966) far removed from the points of application. 2,4,5-T may enter the aquatic environment via surface runoff from treated areas; maximal concentrations in surface water typically occur shortly after application and decrease significantly over time (NRCC 1978). For example, 2,4,5-T in runoff water ranged in concentration from 2 to 3 mg·L^{-1} after a simulated rainfall of 1.3 cm in 1 h, 24 h after the herbicide application. Four months after treatment, the concentration of 2,4,5-T in runoff water was less than 1% of that in the runoff immediately after treatment (Trichell *et al.* 1968).

6.3.12.3.2.3 Environmental Concentrations

Concentrations of 2,4,5-T in surface water are usually in the microgram per litre range. 2,4,5-T was found at concentrations above 1 μg·L^{-1} in 85 of 260 samples of natural waters from Alberta and Saskatchewan in 1972 (Simpkins and Peake 1973). In 1974, eight agricultural watersheds in southern Ontario were monitored for phenoxy herbicides. Four watersheds contained 2,4,5-T, with mean concentrations ranging from 0.15 to 1.2 μg·L^{-1} (Frank *et al.* 1978). Eleven agricultural watersheds were monitored for 2,4,5-T in 1975 in southern Ontario; 2% of the 404 samples collected contained 2,4,5-T, with mean concentrations ranging from less than 0.5 to 0.9 μg·L^{-1} (Frank *et al.* 1978). Environmental concentration ranges for 2,4,5-T in Canadian surface waters are presented in Table 6-117.

A 2-year monitoring program of 20 rivers in the western U.S.A. found that 28 of 331 water samples contained 2,4,5-T at 10-70 μg·L^{-1} (Manigold and Schulze 1969).

Table 6-117. Environmental Concentration Ranges for 2,4,5-T in Canadian Surface Waters

Region	Concentration range[1] (μg·L^{-1})	Number of samples	Sampling year(s)
Pacific	ND[2]-60	196	Prior to 1980
Western	ND-0.04	1494	1980-1985
Central	ND-0.002	4	1980-1981
Atlantic	ND-0.02	50	1980-1985

[1] Detection limit is 0.01 μg·L^{-1}.

[2] ND = not detected.

Source: NAQUADAT 1985.

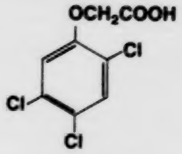

Figure 6-11. 2,4,5-T.

6.3.12.3.2.4 Forms and Fate in the Aquatic Environment

2,4,5-T (Figure 6-11) is a white crystalline solid with a molecular weight of 255.5, a melting point of 153-156°C, a water solubility of 150 mg·L^{-1} at 25°C (Que Hee and Sutherland 1981; Verschueren 1983; Worthing 1983) and a vapour pressure of 0.7 mPa at 25°C (Worthing 1983). It is stable in aqueous solution at pH 5-9 (Worthing 1983).

2,4,5-T is usually formulated as amine salts, alkali metal salts or esters (Ashworth *et al.* 1970), all of which may undergo hydrolysis to the corresponding acid (NRCC 1978).

The hydrolysis of 2,4,5-T esters in moist soils is usually complete within 72 h at 25°C (Smith 1972, 1976). 2,4,5-T esters may also be hydrolyzed under conditions of natural pH and temperature in the aquatic environment. At pH 7, hydrolytic half-lives of approximately 5-30 d at 20°C and 30-180 d at 0°C for various ester formulations have been reported. In addition, sorption of 2,4,5-T to flocculated humic acid was found to accelerate its hydrolysis at low and neutral pH (Struif *et al.* 1975).

2,4,5-T is slowly photooxidized in aqueous solution. Irradiation at 300-450 nm resulted in a 10% loss of 2,4,5-T after 180 h. Photolysis occurred slightly faster at pH 8 than at pH 3. In the presence of compounds such as acetone and riboflavin, the rate of photodegradation increased, with 80% removal in 48 h (Crosby and Wong 1973).

Volatilization of 2,4,5-T from aqueous systems is not expected to be a significant removal process above about pH 4. However, because the hydrolysis of ester formulations may be relatively slow in certain circumstances, some volatilization of the ester may occur (NRCC 1978).

Little information is available on the sorption of 2,4,5-T in aqueous systems. Esters of 2,4,5-T are strongly sorbed to flocculated humic acid at low and neutral pH (Struif *et al.* 1975). Because 2,4,5-T is predominantly anionic in nature at pH 4-9, adsorption to negatively charged soil particles is limited. Partitioning to soils is related primarily to soil organic content; partition coefficients of 0.31-5.3 were measured for soils with organic carbon contents ranging from 0.53 to 14% (NRCC 1978).

In general, 2,4,5-T appears to be more persistent in terrestrial and aquatic environments than are other phenoxy herbicides, such as 2,4-D (NRCC 1978). Half-lives of 20-59 d have been reported for 2,4,5-T in several different soil types (Smith 1972, 1976). Investigations have found that activated sludge systems, using cultures adapted to degrade 2,4-D, could not degrade 2,4,5-T (Struif *et al.* 1975). Ring cleavage of 2,4,5-T in soil suspensions required more than 6 months (Crosby and Wong 1973).

2,4,5-T does not appear to significantly bioaccumulate in the aquatic environment. The octanol/water partition coefficient of 2,4,5-T has been calculated to be 0.533, compared with 64 000 for mixed butyl esters of 2,4,5-T (Kenaga 1974). Calculated bioconcentration factors of 2 (based on partitioning to organic carbon) and 28 (based on 2,4,5-T water solubility) have been reported (Kenaga 1980). Bioconcentration factors of 267 for algae, 180-217 for *Daphnia*, 75 for snail and 25 for mosquitofish were found during a static aquatic ecosystem model study (Isensee 1971). Cumulative storage of 2,4,5-T along the major links in the aquatic food web does not appear to be a general phenomenon (NRCC 1978).

6.3.12.3.2.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Ashworth, R. de B., J. Henriet and J.F. Lovett. 1970. CIPAC Handbook. Vol. 1. Analysis of Technical and Formulated Pesticides. G.R. Shaw (ed.). W. Heffer and Sons Ltd., Cambridge, England. 1079 pp.

Cohen J.M. and C. Pinkerton. 1966. Widespread translocation of pesticides by air transport and rainout. *In* Organic Pesticides in the Environment. Adv. Chem. Ser. No. 60. pp. 163-176. (Cited in Que Hee and Sutherland 1981.)

Crosby, D.G. and A.S. Wong. 1973. Photodecomposition of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in water. J. Agric. Food Chem. 21: 1052-1054.

Environment Canada/Ministère de l'Environnement du Québec. 1984. Les Pesticides en Agriculture au Québec en 1982. Service de la protection de l'environnement/Service de l'assainissement agricole, Montréal, Québec. 134 pp.

Frank, R., H.E. Braun, M. Holdrinet, G.J. Sirons and R.B. Ripley. 1978. Monitoring Stream Water for Pesticides in Eleven Agricultural Watersheds in Southern Ontario, Canada, 1974-1977 (Project 4). International Joint Commission Technical Report, Windsor, Ontario.

Isensee, A.R. 1971. Biomagnification study of 2,4,5-T. Agricultural Environmental Quality Institute. Agricultural Research Center, U.S. Dep. of Agriculture, Beltsville, Maryland. Internal Report. (Cited in NRCC 1978.)

Kenaga, E.E. 1974. 2,4,5-T and derivatives: toxicity and stability in the aquatic environment. Down Earth 29: 137-149. (Cited in NRCC 1978.)

Kenaga, E.E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotoxicol. Environ. Saf. 4: 26-38.

Manigold, D.B. and J.A. Schulze. 1969. Pesticides in selected western streams in a progress report. Pestic. Monit. J. 3: 124-135. (Cited in NRCC 1978.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1978. Phenoxy Herbicides – Their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16075. 440 pp.

Que Hee, S.S. and Sutherland, R.G. 1981. The Phenoxyalkanoic Herbicides. Vol. 1. Chemistry, Analysis and Environmental Pollution. CRC Press, Inc. Boca Raton, Florida. 321 pp.

Simpkins, N.J. and A.A. Peake. 1973. Report on the Chemistry and Biochemistry of Herbicides. Agriculture Canada, Regina, Saskatchewan, March 5-6. (Cited in Que Hee and Sutherland 1981.)

Smith, A.E. 1972. The hydrolysis of 2,4-dichlorophenoxyacetate esters to 2,4-dichlorophenoxyacetic acid in Saskatchewan soils. Weed Res. 12: 364-372. (Cited in NRCC 1978.)

Smith, A.E. 1976. The hydrolysis of herbicidal phenoxyalkanoic esters to phenoxyalkanoic acids in Saskatchewan soils. Weed Res. 16: 19-22. (Cited in NRCC 1978.)

Statistics Canada. 1978. Sales of Pest Control Products by Canadian Registrants 1977. Catalogue No. 46-212.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Struif, B., L. Weil and K.E. Quentin. 1975. The behavior of herbicidal phenoxy acetic acids and their esters in waters. Vom Wasser 45: 53-73. (Cited in Que Hee and Sutherland 1981.)

Trichell, D.W., H.L. Morton and M.G. Merkle. 1968. Loss of herbicides in runoff water. Weed Sci. 16: 447-449. (Cited in NRCC 1978.)

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Weibel, S.R., R.B. Weidner, A.G. Christianson and J.M. Cohen. 1965. Pesticides and other contaminants from rainfall and runoff. *In* 85th Annu. Conf. Am. Water Works Assoc., June 27-July 2, Portland, Oregon. (Cited in Que Hee and Sutherland 1981.)

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 502.

6.3.12.3.3 2,4,5-TP

6.3.12.3.3.1 Uses and Production

2,4,5-Trichlorophenoxypropanoic acid, known as 2,4,5-TP (silvex or fenoprop), was originally introduced as a herbicide for controlling weeds in rivers and lakes in 1952. It is used to control woody plants, broadleaf herbaceous weeds and aquatic weeds, and also acts as a selective postemergence herbicide in rice and bluegrass turf. It is applied to sugarcane fields to control wild lettuce, chicory, nightshade and other weeds not susceptible to 2,4-D. Rangeland improvement programs use 2,4,5-TP for bush control, especially against blackjack, sand shinnery oaks, yucca and salt cedar. It controls alligator weeds in ditches and riverbanks, as well as such 2,4-D-tolerant weeds as chickweeds, spurges and black medic in turf (NAS 1977; Weed Science Society of America 1979).

In 1981 and 1983, 24 and 1 t, respectively, of formulated 2,4,5-TP were imported into Canada. No imports of formulated 2,4,5-TP were reported in 1982. No imports were reported for technical-grade 2,4,5-TP in 1981, 1982 and 1983 (Statistics Canada 1983).

Additional names for 2,4,5-TP[*] include Aqua-Vex; Ded-Weed; Fruitone T; Garlon; Kuron; Kurosal; O-X-D; Silvi-Rhap; Weedone; Silvex; and Fenoprop[*] (Weed Science Society of America 1979; Statistics Canada 1983).

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[*] Names registered for use in Canada (Agriculture Canada 1984).

6.3.12.3.3.2 Sources and Pathways for Entering the Aquatic Environment

2,4,5-TP can enter the environment in the effluents of herbicide manufacturing and packaging plants and other related industries. Another source of 2,4,5-TP in the aquatic environment is municipal effluents (McNeely *et al.* 1979).

2,4,5-TP drifts into the atmosphere during its application, although contamination of surface water is chiefly through surface runoff and direct application (NRCC 1978; McNeely *et al.* 1979).

6.3.12.3.3.3 Environmental Concentrations

A study of 20 rivers in the western U.S.A. revealed that 14 of 331 water samples contained 2,4,5-TP in the concentration range of 10-200 $\mu g \cdot L^{-1}$ (Manigold and Schulze 1969).

A study of eight agricultural watersheds in Ontario in 1974 showed that 2,4,5-TP was present in 2% of the samples taken, but only in trace quantities ($<0.1\ \mu g \cdot L^{-1}$) (Frank *et al.* 1978). Investigations of farm ponds and wells in Ontario for suspected phenoxy herbicide contamination indicated that 4-10% contained detectable levels of MCPA (4-chloro-2-methylphenoxyacetic acid), mecaprop, dichloroprop and/or 2,4,5-TP (Frank 1970-1974).

Environmental concentration ranges for 2,4,5-TP in Canadian surface waters are presented in Table 6-118.

6.3.12.3.3.4 Forms and Fate in the Aquatic Environment

2,4,5-TP (2,4,5-trichlorophenoxypropanoic acid) (Figure 6-12) is a colourless powder with a melting point of 179-181°C and a water solubility of approximately 140 $mg \cdot L^{-1}$ at 20°C (Worthing 1983). Commercial formulations of 2,4,5-TP are generally composed of the salts or esters of the acid. The ester formulations have low water solubility, although they are highly soluble in petroleum solvents (NAS 1977; Weed Science Society of America 1979).

2,4,5-TP is relatively stable chemically, although its salts and esters readily undergo hydrolysis to yield the acid. Hydrolysis of esters in water is rapid; 50% conversion in 5-8 h and complete conversion in 33-49 h in pond water have been observed (Bailey *et al.* 1970). Hydrolysis also occurs in moist soils at 25°C, with no ester remaining after 24 h (Smith 1976).

2,4,5-TP does not photodegrade as readily as 2,4-D; it is slowly degraded in water, with 10% removal after 180 h of artificial irradiation. The main photoproduct appears to be 2,4,5-trichlorophenol. Under natural sunlight conditions, photodegradation is very slow (Crosby and Wong 1973).

Like other phenoxy herbicides, 2,4,5-TP may be adsorbed by surfaces in terrestrial and aquatic systems; however, because it is anionic in the range of pH 4-9, its adsorption onto negatively charged soil particles is not extensive. Soil partition coefficients vary from approximately 0.3 to 5, and are positively related to soil organic content (Manigold and Schulze 1969).

Microbial degradation of 2,4,5-TP in soil and water requires optimum conditions of moisture and temperature. In general, biological degradation is less likely in colder or drier soils. Similarly, breakdown is inhibited at moisture levels in excess of the field capacity or at temperatures above 35°C (NRCC 1978). Soils with higher organic content usually support a higher microbiological population, and therefore could support an increased rate of herbicide breakdown. In general, microbial degradation of 2,4,5-TP is slower than that of 2,4-D. Half-lives up to approximately 3 months have been observed in some Saskatchewan soils (NRCC 1978).

Table 6-118. Environmental Concentration Ranges for 2,4,5-TP in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	5	2	Prior to 1980
Western	4	1339	1981
Central	<4-55	104	Prior to 1980

[1] Detection limit is 4 $ng \cdot L^{-1}$.

Source: NAQUADAT 1985.

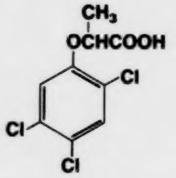

Figure 6-12. 2,4,5-TP.

2,4,5-TP does not appear to significantly bioaccumulate in the aquatic environment; bioconcentration factors range from about 25 to 270, depending upon the aquatic organism tested. Higher values have been reported for aquatic plants and plankton; however, 2,4,5-TP does not appear to biomagnify in the aquatic food web (NRCC 1978; Que Hee and Sutherland 1981).

6.3.12.3.3.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Bailey, G.W., A.D. Thruston, Jr., J.D. Pope, Jr. and D.R. Cochrane. 1970. The degradation kinetics of an ester of silvex and the persistence of silvex in water and sediment. Weed Sci. 18: 413-419.

Crosby, D.G. and A.S. Wong. 1973. Photodecomposition of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in water. J. Agric. Food Chem. 21: 1052-1054.

Frank, R. 1970-1974. Annual Report – Analysis of Samples Connected with Herbicide Damage Investigations. Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food, Guelph, Ontario. (Cited in NRCC 1978.)

Frank, R., H.E. Braun, M. Holdrinet, G.J. Sirons and B.D. Ripley. 1978. Monitoring Stream Water for Pesticides in Eleven Agricultural Watersheds in Southern Ontario, Canada, 1974-1977 (Project 4). International Joint Commission Technical Report, Windsor, Ontario.

Manigold, D.B. and J.A. Schulze. 1969. Pesticides in selected western streams in a progress report. Pestic. Monit. J. 3: 124-135. (Cited in NRCC 1978.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NRCC. 1978. Phenoxy Herbicides – Their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16075. 440 pp.

Que Hee, S.S. and R.G. Sutherland. 1981. The Phenoxyalkanoic Herbicides. Vol. 1. Chemistry, Analysis and Environmental Pollution. CRC Press, Inc., Boca Raton, Florida. 321 pp.

Smith, A.E. 1976. The hydrolysis of herbicidal phenoxyalkanoic esters to phenoxyalkanoic acids in Saskatchewan soils. Weed Res. 16: 19-22.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Weed Science Society of America. 1979. Herbicide Handbook. 4th edition. Champaign, Illinois.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 262.

6.3.12.4 Organochlorine Compounds

6.3.12.4.1 Aldrin

6.3.12.4.1.1 Uses and Production

The original uses of aldrin were as a pesticide for control of soil, fruit and vegetable pests, as well as for specific control of grasshoppers, locusts and termites. Its current use in the United States is restricted to those situations in which there is no effluent discharge, e.g. in ground injection for termite control (U.S. EPA 1980).

Ciba-Geigy Canada Ltd., Mississauga, Ontario, is the only registered agent that can import aldrin into Canada. Its supplier is Shell International Chemical Company, London, England, which markets aldrin under the name "Shell Aldrin 40EC Insecticide" (Agriculture Canada 1984). No imports were reported for the years 1981-1983 (Statistics Canada 1983, 1984). In Ontario, a small amount of aldrin is still used for termite control (Ralston 1985).

Additional names for aldrin include Alarite; Aldrec; Aldrex*; aldrine; Aldrosol*; Algran; Compound 118; Aldrite*; Drinox; HHDN; Octalene; Seedrin Liquid and Soildrin (McNeely *et al.* 1979).

6.3.12.4.1.2 Sources and Pathways for Entering the Aquatic Environment

Aldrin is applied to soil and foliage by injection or aerial spraying. Leaching of aldrin is thought to be minimal, with soil erosion and sediment transport the major pathways for entering the aquatic environment (U.S. EPA 1980). Trace concentrations of 1-2 $\mathrm{ng \cdot L^{-1}}$ were found for aldrin and dieldrin in rainfall. Comparable concentrations were observed for accumulated snowfalls in the Great Lakes region (Strachan and Huneault 1979).

6.3.12.4.1.3 Environmental Concentrations

Various studies have reported concentrations of aldrin in surface waters ranging from 0.1 to 85 $\mathrm{ng \cdot L^{-1}}$ (Lichtenberg *et al.* 1970; U.S. EPA 1976; U.S. EPA 1982). No direct measurements of aldrin residues in aquatic animals are available (U.S. EPA 1980).

Little information is available on environmental residue levels of aldrin, probably because it is rapidly transformed to dieldrin in the environment (U.S. EPA 1979, 1980). One study reported that 40% of the aldrin added to raw river water was detectable after 4 weeks of incubation (Eichelberger and Lichtenberg 1971).

Environmental concentration ranges for aldrin in Canadian surface waters are presented in Table 6-119.

6.3.12.4.1.4 Forms and Fate in the Aquatic Environment

Aldrin, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*exo*-1,4-*endo*-5,8-dimethanonaphthalene (Figure 6-13), has a water solubility of 27 $\mathrm{\mu g \cdot L^{-1}}$ at 25-29°C (Park and Bruce 1968) and a vapour pressure of 3.1 mPa at 25°C (Martin 1972). Technical-grade aldrin contains 95% active ingredient (Ashworth *et al.* 1970).

Biotransformation, volatilization, bioaccumulation and perhaps indirect photolysis may all play significant roles in the removal of aldrin from the water column (U.S. EPA 1979).

Hydrolysis is not expected to be an important process in the aquatic environment. Although very few data are available, it is expected that sorption processes play a relatively minor role (U.S. EPA 1979). In general, soil sorption coefficients are small ($\approx$400) (Kenaga and Goring 1978).

Photolysis appears to be important in the degradation of aldrin, the major product being photoaldrin. The half-life of aldrin that was converted to photoaldrin in a sample of natural water in the presence of sunlight was determined to be 1.1 d (Singmaster 1975). Studies in nonaqueous systems showed that aldrin is converted to photoaldrin (Rosen and Carey 1968; Ivie and Casida 1971). It has also been demonstrated that dieldrin (see Section 6.3.12.4.5) is produced from aldrin via photolysis. The photolysis of aldrin in sterile paddy water yielded 25% dieldrin in 36 h. No photoaldrin was detected (Ross and Crosby 1975).

Laboratory measures of volatilization under simulated wind and temperature conditions have yielded volatilization half-lives ranging from as short as 0.4 h (Singmaster 1975) to a maximum of 7.7 d (Mackay and Wolkoff 1973; Mackay and Leinonen 1975).

Short-term bioconcentration factors measured in terrestrial-aquatic microcosm studies are in the order of 10^3-10^4 (Metcalf *et al.* 1973). Biomagnification is not considered to be important because of aldrin's rapid conversion to dieldrin in aquatic biota (U.S. EPA 1979).

Biotransformation appears to be the most important of all processes governing the fate of aldrin in the aquatic environ-

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* Names registered for use in Canada (Agriculture Canada 1984).

Table 6-119. Environmental Concentration Ranges for Aldrin in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Central	<1	314	1980-1985
Atlantic	<1-1	38	1980-1984

[1] Detection limit is 1 $ng \cdot L^{-1}$.

Source: NAQUADAT 1985.

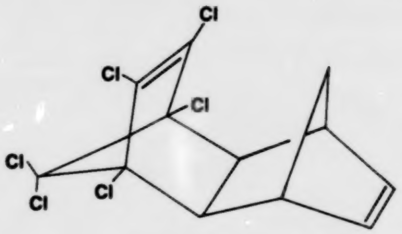

Figure 6-13. Aldrin.

ment, converting the parent compound via epoxidation to dieldrin (U.S. EPA 1979). Although the data do not permit rate calculations (U.S. EPA 1979), transformation processes have been demonstrated in virtually all organisms, from microbes, algae and invertebrates to fish, birds and mammals (Rosenblatt *et al.* 1975; Sanborn *et al.* 1977). For example, a biological half-life of 7 d has been reported for aldrin in Atlantic salmon (*Salmo salar*) (Addison et *al.* 1976). The transformation process appears to be virtually complete, with conversions of aldrin to dieldrin consistently above 90% (Metcalf *et al.* 1973).

5.3.12.4.1.5 References

Addison, R.F., M.E. Zinck and J.R. Leahy. 1976. Metabolism of single and combined doses of ^{14}C-aldrin and ^{3}H-*p,p'*-DDT by Atlantic salmon (*Salmo salar*) fry. J. Fish. Res. Board Can. 33: 2073-2076.

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Ashworth, R. de B., J. Henriet and J.F. Lovett. 1970. CIPAC Handbook. Vol. 1. Analysis of Technical and Formulated Pesticides. G.R. Raw (ed.). Collaborative International Pesticides Analytical Council Limited, W. Heffer and Sons Ltd., Cambridge, England. 1079 pp.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Ivie, G.W. and J.E. Casida. 1971. Sensitized photodecomposition and photosensitizer activity of pesticide chemicals exposed to sunlight on silica gel chromatoplates. J. Agric. Food Chem. 19: 405-409. (Cited in U.S. EPA 1979.)

Kenaga, E.E. and C.A.I. Goring. 1978. Relationship between water solubility, soil-sorption, octanol-water partitioning and bioconcentration of chemicals in biota. *In* Proc. Am. Soc. Test. Mater. 3rd Aquat. Toxicol. Symp., New Orleans, Louisiana. p. 63.

Lichtenberg, J.J., J.W. Eichelberger, R.C. Dressman and J.E. Longbottom. 1970. Pesticides in surface waters of the United States – A five-year summary, 1964-1968. Pestic. Monit. J. 4: 71-86. (Cited in U.S. EPA 1980.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Mackay, D. and A.W. Wolkoff. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7: 611-614.

Martin, H. 1972. Pesticide Manual. 3rd edition. British Crop Protection Council, Worcester, England.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

Metcalf, R.L., I.P. Kapoor, P.-Y. Lu, C.K. Schuth and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4: 35-44.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Park, K.S. and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor epoxide. J. Econ. Entomol. 61: 770-774.

Ralston, J. 1985. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Rosen, J.D. and W.F. Carey. 1968. Preparation of the photoisomers of aldrin and dieldrin. J. Agric. Food Chem. 16: 536-537. (Cited in U.S. EPA 1979.)

Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul and D.R. Cogley (eds.). 1975. Appendix K – Aldrin/dieldrin. *In* Problem Definition Studies on Potential Environmental Pollutants. II. Physical, Chemical, Toxicological, and Biological Properties of 16 Substances. U.S. Army Medical Bioengineering Research and Development Laboratory, Frederick, Maryland. Tech. Rep. 7509. 290 pp.

Ross, R.D. and D.G. Crosby. 1975. The photooxidation of aldrin in water. Chemosphere 4: 277-282.

Sanborn, J.R., B.M. Francis and R.L. Metcalf. 1977. The Degradation of Selected Pesticides in Soil: A Review of the Published Literature. U.S. Environmental Protection Agency, Washington, D.C. EPA/600/9-77/022.

Singmaster, J.A., III. 1975. Environmental Behavior of Hydrophobic Pollutants in Aqueous Solutions. Ph.D. Thesis. Univ. California, Davis, California. University Microfilms, Ann Arbor, Michigan. Order No. 76-14, 237. (Diss. Abstr. Int. B 1976, 36(12, pt. 1): 6206-6207.) (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Strachan, W.M.J. and C.J. Edwards. 1984. Organic pollutants in Lake Ontario. *In* Toxic Contaminants in the Great Lakes. Advances in Environmental Science and Technology. Vol. 14. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, Toronto, Ontario. pp. 239-264.

Strachan, W.M.J. and H. Huneault. 1979. Polychlorinated biphenyls and organochlorines in the Great Lakes region. J. Great Lakes Res. 5: 61-68.

U.S. EPA. 1976. National Interim Primary Drinking Water Regulations. U.S. Environmental Protection Agency. EPA-570/9-76-003. (Cited in U.S. EPA 1980.)

U.S. EPA. 1979. Aldrin. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 21-1 to 21-13.

U.S. EPA. 1980. Ambient Water Quality Criteria for Aldrin/Dieldrin. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-019.

U.S. EPA. 1982. STORET. STOrage and RETrieval of Water Quality Data: A Computerized Information System. U.S. Environmental Protection Agency, Washington, D.C. (Cited in Strachan and Edwards 1984.)

6.3.12.4.2 Chlordane

6.3.12.4.2.1 Uses and Production

Chlordane is used to control a variety of insects and insect larvae on ornamentals, vegetables, bulbs, strawberries, lawns and turfs. It is also used to control wood-boring insects in housing and other buildings. Chlordane's usage is limited to once every 4 years for agricultural applications or once per crop rotation cycle (Agriculture Canada 1985a). As of December 1985, the above uses of chlordane were suspended except for the control of subterranean insects (Agriculture Canada 1985b).

Chlordane (formulated or technical grade not specified) was imported into Canada in 1981, 1982 and 1983 in the amounts of 43, 27 and 53 t, respectively (Statistics Canada 1983, 1984). In 1977, 120.6 t of chlordane (not including fungicides) were sold in Canada (Agriculture Canada 1984).

Additional names for chlordane that are used in Canada include Chlor-Kil; Coradane; and Chlordan (Agriculture Canada 1984).

6.3.12.4.2.2 Sources and Pathways for Entering the Aquatic Environment

The presence of chlordane in the aquatic environment is directly related to the manufacturing process and pesticide application on crops. Chlordane can reach the aquatic environment through drift from aerial spraying, surface runoff, percolation and subsurface seepage from treated lands, careless application or spillage, sewage discharge and industrial effluents (McNeely *et al.* 1979).

In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of chlordane were observed in 15 samples (Environment Canada 1984). In 1979 and 1980 surveys of contaminants in treated water at treatment plant intakes in three cities along the Niagara River, δ-chlordane was detected in only 1 of 29 samples (detection limit 1 $ng \cdot L^{-1}$); α-chlordane*, however, was not detected in any of the 29 samples analyzed for the pesticide (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.12.4.2.3 Environmental Concentrations

Concentrations of chlordane and its isomers in Canadian surface waters have been reported in several areas and regions. Environmental concentration ranges for chlordane in Canadian surface waters are presented in Table 6-120. Concentration ranges of δ-chlordane in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-121; α-chlordane, however, was not detected in any of the 60 samples taken in the same years (Environment Canada/Ontario Ministry of the Environment 1981).

Table 6-120. Environmental Concentration Ranges for Chlordane in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
cis-chlordane			
Pacific	ND[2]-32	116	Prior to 1980
Western	ND	1352	1980-1985
Central	ND	322	1980-1985
Atlantic	ND	42	1980-1985
trans-chlordane			
Pacific	ND	111	Prior to 1980
Western	ND	1352	1980-1985
Central	ND	324	1980-1985
Atlantic	ND	42	1980-1985

[1] Detection limit is 5 $ng \cdot L^{-1}$.

[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-121. Concentration Ranges of δ-Chlordane in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water During 1979 and 1980

Location	Year	Total number of samples	Number of samples with detectable concentrations	Concentration range ($ng \cdot L^{-1}$)
Niagara-on-the-Lake	1979	7	0	ND[1]
	1980	12	1	ND-3
Niagara Falls	1979	7	0	ND
	1980	11	1	ND-2
Fort Erie	1979	7	1	ND-1
	1980	11	1	ND-1
St. Catharines	1980	5	0	ND

[1] ND = not detected; detection limit is 1 $ng \cdot L^{-1}$.

Source: Environment Canada/Ontario Ministry of the Environment 1981.

6.3.12.4.2.4 Forms and Fate in the Aquatic Environment

Chlordane, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene, is composed of mixtures of stereoisomers, with the *cis*- and *trans*-forms predominating (Figure 6-14) (U.S. EPA 1979).

Technical-grade chlordane is composed of a mixture of various chlorinated hydrocarbons, with a typical composition of approximately 24% *trans*-isomer, 19% *cis*-isomer, 10% heptachlor, 21% chlordene isomers, 7% nonachlor and 18.5% related chlorinated hydrocarbon compounds (Brooks 1974). Chlordane has a vapour pressure of 1.3 mPa at 25°C (Brooks 1974), a water solubility of 0.056 $mg \cdot L^{-1}$ (Martin 1972) and a calculated log octanol/water partition coefficient of 2.78 (Martin 1972).

Among the various processes regulating the fate of chlordane, the most significant in the aquatic environment are sorption, volatilization and bioaccumulation (U.S. EPA 1979).

Hydrolysis experiments indicate that chlordane is stable in water (Bevenue and Yeo 1969; Eichelberger and Lichtenberg

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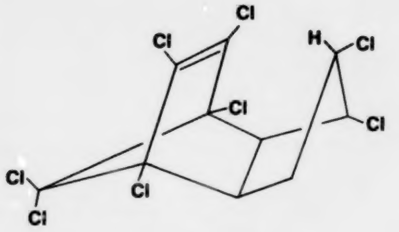
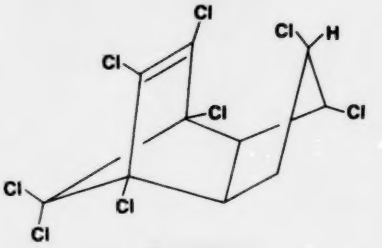
* *Cis*- and *trans*-chlordane have been called α- and δ-chlordane, respectively, in some reports, and β- and δ-chlordane, respectively, in others (U.S. EPA 1979).



Cis-chlordane



Trans-chlordane

Figure 6-14. *Cis-* and *trans*-chlordane.

1971). No information is available on its oxidation in aquatic systems (U.S. EPA 1979).

In the absence of sediments, chlordane is volatilized from water, with a 40-50% loss in 6 weeks and 60% loss in 12 weeks. Laboratory experiments on the volatilization of *trans*-chlordane at concentrations of $25\ \mu g \cdot L^{-1}$ in water at 9°C showed losses of 34% in a 3-d period. In a similar experiment with *cis*-chlordane, 24% was lost. When concentrations of *cis*- and *trans*-chlordane at $25\ \mu g \cdot L^{-1}$ were placed in flasks containing samples of water and sediment, more than 80% of the chlordane initially added was recovered from the sediments after 12 weeks. These experiments indicate that sorption to sediments predominates over volatilization in the removal of chlordane from the water column (Oloffs *et al.* 1972, 1973; Oloffs and Albright 1974).

Bioaccumulation is also an important removal process for chlordane in the aquatic environment. Bioconcentration factors for bacteria, daphnids and fish are in the order of 10^3-10^4 (U.S. EPA 1979). One study found that the *trans*-isomer was eliminated from northern redhorse suckers (*Moxostoma macrolepidotum*) about 1.8 times faster than the *cis*-isomer. Elimination half-lives of *cis*- and *trans*-chlordane of 60 and 33 d, respectively, were found (Roberts *et al.* 1977). An approximate elimination half-life of 35 d was estimated for *cis*-chlordane in goldfish (*Carassius auratus*) (Ducat and Khan 1979).

Very little information is available on the biotransformation of chlordane in aquatic systems. Chlordane was found to be persistent in both flooded and nonflooded soils and was comparable in persistence to dieldrin (Castro and Yoshida 1971; Watanabe 1973). In terrestrial-aquatic microcosm studies, some metabolism of chlordane was found (Sanborn *et al.* 1976). Bluegill sunfish (*Lepomis macrochirus*) metabolized less than 7% of the chlordane taken up within 48 h; hydroxylated and conjugated derivatives were the primary products (Sudershan and Khan 1980). Oxychlordane, the persistent and toxic metabolite of chlordane, is the major metabolite produced in mammalian systems (Schwemmer *et al.* 1970), and is the major terminal residue in animal tissues and milk (Barnett and Dorough 1974).

6.3.12.4.2.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985a. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Agriculture Canada. 1985b. Trade Memorandum. T-1-250. Pesticides Division, Food Production and Inspection Branch, Ottawa. 6 pp.

Barnett, J.R. and H.W. Dorough. 1974. Metabolism of chlordane in rats. J. Agric. Food Chem 22: 612-619.

Bevenue, A. and C.Y. Yeo. 1969. Gas chromatographic characteristics of chlordane. II. Observed compositional changes of the pesticide in aqueous and nonaqueous environments. J. Chromatogr. 42: 45-52.

Brooks, G.T. 1974. Chlorinated Insecticides. Vol. 1. Technology and Applications. CRC Press, Inc., Cleveland, Ohio. 249 pp. (Cited in U.S. EPA 1979.)

Castro, T.F. and T. Yoshida. 1971. Degradation of organochlorine insecticides in flooded soils in the Philippines. J. Agric. Food Chem. 19: 1168-1170. (Cited in U.S. EPA 1979.)

Ducat, D.A. and M.A.Q. Khan. 1979. Absorption and elimination of ^{14}C-*cis*-chlordane and ^{14}C-*cis*-photo-chlordane by goldfish (*Carassius auratus*). Arch. Environ. Contam. Toxicol. 8: 409-417.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Martin, H. 1972. Pesticide Manual. 3rd edition. British Crop Protection Council, Worcester, England. (Cited in U.S. EPA 1979.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Oloffs, P.C. and L.J. Albright. 1974. Transport of some organochlorines in British Columbia waters. *In* Proc. Int. Conf. on the Transportation of Persistent Chemicals in Aquatic Ecosystems. Vol. 1. Ottawa. pp. 89-92.

Oloffs, P.C., L.J. Albright and S.Y. Szeto. 1972. Fate and behavior of five chlorinated hydrocarbons in three natural waters. Can. J. Microbiol. 18: 1393-1398.

Oloffs, P.C., L.J. Albright, S.Y. Szeto and J. Lau. 1973. Factors affecting the behavior of five chlorinated hydrocarbons in two natural waters and their sediments. J. Fish. Res. Board Can. 30: 1619-1623.

Roberts, J.R., A.S.W. De Frietas and M.A.J. Bidney. 1977. Influence of lipid pool size on bioaccumulation of the insecticide chlordane by northern redhorse suckers (*Moxostoma macrolepidotum*). J. Fish. Res. Board Can. 34: 89-97.

Sanborn, J.R., R.L. Metcalf, W.N. Bruce and P.-Y. Lu. 1976. The fate of chlordane and toxaphene in a terrestrial-aquatic model ecosystem. Environ. Entomol. 5: 533-538.

Schwemmer, B., W.P. Cochrane and P.B. Polen. 1970. Oxychlordane, animal metabolite of chlordane: Isolation and synthesis. Science 169: 1087.

Statistics Canada. 1978. Sales of Pest Control Products by Canadian Registrants 1977. Catalogue No. 46-212.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Sudershan, P. and M.A.Q. Khan. 1980. Metabolism of ^{14}C-*cis*-chlordane and ^{14}C-*cis*-photochlordane in bluegill sunfish. J. Agric. Food Chem. 28: 291-296.

U.S. EPA. 1979. Chlordane. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 22-1 to 22-13.

Watanabe, I. 1973. Decomposition of pesticides by soil microorganisms – Special emphasis on flooded soil conditions. JARQ 7: 15-18. (Cited in U.S. EPA 1979.)

6.3.12.4.3 DDD

6.3.12.4.3.1 Uses and Production

DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) is not registered in Canada for use as a pesticide under the Pest Control Products Act (Agriculture Canada 1984). However, it might appear as a contaminant in other pesticide formulations, such as DDT. No imports were reported for DDD in 1981, 1982 and 1983 (Statistics Canada 1983, 1984).

Additional names for DDD include TDE; Rhothane (U.S. EPA 1979); tetrachlorodiphenylethane; dichlorodiphenyldichloroethane; *p,p'*-DDD; and *p,p'*-TDE (Windholtz *et al.* 1983).

6.3.12.4.3.2 Sources and Pathways for Entering the Aquatic Environment

DDD enters the environment through its manufacture and application, and as a metabolite of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT). DDT has a number of breakdown products, of which DDD and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene) (Windholtz *et al.* 1983) are the most ubiquitous (Waldbott 1978). The pathways for general environmental contamination by DDD include atmospheric dispersion, wind and water erosion of soil and transport while sorbed onto soil particles in the silt of streams, estuaries and oceans. DDD can also move through the environment as residues in biological tissues, especially fish and wildfowl (Lykken 1971).

6.3.12.4.3.3 Environmental Concentrations

NAQUADAT data on DDD levels from various regions in Canada are presented in Table 6-122.

6.3.12.4.3.4 Forms and Fate in the Aquatic Environment

Commercial preparations of DDD consist of more than one isomer, with the *p,p'*-isomer being the major component (Figure 6-15) (U.S. EPA 1979).

The major known removal processes for DDD in the aquatic environment include volatilization, sorption to sediments and biota and bioaccumulation (U.S. EPA 1979).

DDD has a low solubility in water (20-90 $\mu g \cdot L^{-1}$), but may be readily adsorbed to organic material (calculated log octanol/water partition coefficient of 5.99) (U.S. EPA 1979). Direct photolysis is expected to be slower than that of DDT.

Table 6-122. Environmental Concentration Ranges for DDD in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<1-7	457	Prior to 1980
Western	1-2	1352	1980-1981
Central	0.4-1	310	1980-1982
Atlantic	<1-1	42	1983-1984
	5[2]	1	Prior to 1980

[1] Detection limit is 1 $ng \cdot L^{-1}$.

[2] Analysis for *o,p'*-DDD only; otherwise *p,p'*-DDD was sampled for.

Source: NAQUADAT 1985.

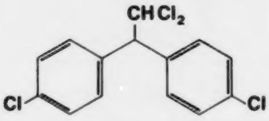


Figure 6-15. *p,p'*-DDD.

Likewise, hydrolysis is relatively insignificant; a hydrolytic half-life of 190 years at pH 5 and 27°C has been reported (Wolfe *et al.* 1977).

Data suggest that the volatilization rate of DDD from aquatic environments is about one-third the rate for DDT (Singmaster 1975). Therefore, through volatilization, DDD will probably have a half-life ranging from 1 d to less than a month (U.S. EPA 1979). Although no specific data are available, sorption to sediments is considered to be an important removal process for DDD in aquatic systems. Sorption coefficients are probably similar to those for DDT (~10^5).

DDD is quite resistant to chemical transformations in aquatic environments, and, although slow, biotransformation is probably the process resulting in the ultimate degradation of DDD in the environment (U.S. EPA 1979). Sorption to biota and bioaccumulation are also important removal processes for DDD. Bioconcentration factors range from 10^3 to 10^5 (U.S. EPA 1979). Concentration factors of 80 000 have been reported for fish-eating birds, and 85 000 for predaceous fish (Rudd 1964).

6.3.12.4.3.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Lykken, L. 1971. Chemical control of pests. Chemistry 44: 18-21.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rudd, R.L. 1964. Pesticides in the Living Landscape. The University of Wisconsin Press, Madison, Wisconsin. 320 pp.

Singmaster, J.A., III. 1975. Environmental Behavior of Hydrophobic Pollutants in Aqueous Solutions. Ph.D. Thesis. Univ. California, Davis, California. University Microfilms, Ann Arbor, Michigan. Order No. 76-14, 237. (Diss. Abstr. Int. B 1976, 36(12, Pt. 1): 6206-6207.) (Cited in U.S. EPA 1979).

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. DDD. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 23-1 to 23-10.

Waldbott, G.L. 1978. Health Effects of Environmental Pollutants. The C.V. Mosby Co., St. Louis, Missouri. 350 pp.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

Wolfe, N.L., R.G. Zepp, D.F. Paris, G.L. Baughman and R.C. Hollis. 1977. Methoxychlor and DDT degradation in water: Ratio and products. Environ. Sci. Technol. 11: 1077-1081.

6.3.12.4.4 DDT

6.3.12.4.4.1 Uses and Production

DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was the first of a series of chlorinated hydrocarbons manufactured as insecticides. DDT was first synthesized in 1874; its use began in 1942 and 1943 when its effectiveness as an insecticide was demonstrated during World War II (Keller 1970). DDT has been used extensively throughout the world for public health and agricultural programs because of its efficiency as a broad-spectrum insecticide and its low cost to manufacture (U.S. EPA 1980). DDT has also been used to treat woolen garments as a mothproofing agent (West 1966).

In 1964, about 1.6×10^6 t of DDT had been produced worldwide; approximately 50% of this production was in the United States (Keller 1970). The U.S.A. banned the use of DDT in 1972 (U.S. EPA 1980).

DDT is registered for use in Canada, but is under federal-provincial restrictions. Sanex Chemicals Ltd., Mississauga, Ontario, is the only company with DDT registration in Canada. It markets the product called "Sanex Rodentrak" that is used to kill rodents and bats (Agriculture Canada 1984).

In 1982, 7 t of formulated DDT was imported into Canada from the U.S.A.; no imports were reported for 1981 or 1983. In 1981, 45.4 kg of technical-grade DDT were imported from the U.S.A.; no imports were reported for 1982 or 1983 (Statistics Canada 1983, 1984).

Additional names for DDT include dichlorodiphenyltrichloroethane; chlorophenothane; dicophane; pentachlorin; *p,p'*-DDT; Agritan; Gesapon; Gesarex; Gesarol; Guesapon; Neocid (Windholtz *et al.* 1983); Anofex; Anofox; chlorophenothene; Dedelco; Didimac; Dinocide; Genitox; Guesarol; Gyron; Ixodex; Kopsol; Neocide; Neocidol; Rukseam; and Zerdane (McNeely *et al.* 1979; Agriculture Canada 1984).

6.3.12.4.4.2 Sources and Pathways for Entering the Aquatic Environment

DDT may enter the aquatic environment through its manufacture and application (Keller 1970; U.S. EPA 1980). The pathways for general environmental contamination by DDT include atmospheric dispersion, wind and water erosion of soil and transport while sorbed onto soil particles in the silt of streams, estuaries and oceans. According to estimates, only half the pesticide released during aerial spraying programs actually reaches its destination. The rest either drifts and settles over adjacent lands, or is carried into the atmosphere to be eventually deposited in areas remote from the source (Keller 1970).

6.3.12.4.4.3 Environmental Concentrations

DDT is very persistent in the environment (Rudd 1964; U.S. EPA 1979, 1980). In the late 1960's, it was estimated that about 454 000 t of DDT were circulating in the biosphere. In the early 1970's, agricultural soils in the United States contained an average of 1.68 kg·ha^{-1} (Waldbott 1978). In one study of 12 apple orchards after 6 years of spraying, DDT accumulated in the soils to a concentration of 39.23-126.60 kg·ha^{-1} under the trees (Rudd 1964). Because of the stability and insolubility of DDT and its related compounds, as much as 50% can remain in the soil 10-15 years after application (Keller 1970).

Water becomes saturated with as little as 1.2 μg·L^{-1} DDT (Waldbott 1978). The concentrations of DDT reported in Canadian surface waters in the 1970's range from not detectable to 397 ng·L^{-1} (Health and Welfare Canada 1980). The concentration at one location several hours after DDT spraying was 17 μg·L^{-1} (Yule and Tomlin 1970). Ottawa drinking water was reported as containing 0.05 ng·L^{-1} (McNeil *et al.* 1977), whereas a background level of 0.5 μg·L^{-1} was reported for a tributary of the Miramichi River (Yule and Tomlin 1970). More Canadian environmental concentrations of DDT are presented in Table 6-123.

DDT has been detected in biological tissues of numerous fish species, fish-eating birds and humans. Examples of maximum concentrations are given in Table 6-124.

DDE, a primary metabolite of DDT, has also been found in surface waters. Environmental concentration ranges for *p,p'*-DDE in Canadian surface waters are presented in Table 6-125.

6.3.12.4.4.4 Forms and Fate in the Aquatic Environment

Preparations of DDT consist primarily of two isomers (Figure 6-16).

Technical-grade DDT may contain 70-73% of the *p,p'*-isomer and 12-21% of the *o,p'*-isomer (U.S. EPA 1979). In addition, DDT has several derivatives or metabolites. Those most frequently found in nature are DDD (TDE), 1,1'-dichloro-2,2-bis-(4-chlorophenyl)ethane, and DDE, 1,1'-dichloro-2,2-bis-(4-chlorophenyl)ethylene, both of which are toxic, persistent in the environment and have widespread occurrence (Figure 6-17) (Waldbott 1978; U.S. EPA 1980).

Because *p,p'*-DDT has a low solubility in water (<1-25 μg·L^{-1}, depending on the presence of other materials in water), the dominant nondegradative transport mechanisms in aquatic environments are volatilization, sorption to biota and sediments and bioaccumulation (Waldbott 1978; U.S. EPA 1979). The ultimate transformation and loss of DDT and its related compounds from the aquatic environment are probably by biotransformation and possibly indirect photolysis (U.S. EPA 1979).

Direct photolysis of DDT in aqueous solutions is very slow; the half-life of DDT is probably longer than 150 years (Zepp *et al.* 1976). However, the half-life of DDT from indirect photolysis in natural water may be about a week, depending upon the presence of photosensitizers (Singmaster 1975). Half-lives are

Table 6-123. Environmental Concentration Ranges for DDT in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
p,p'-DDT			
Pacific	<4-12	489	Prior to 1980
Western	<1-4	1352	1980-1985
Central	0.4-12	316	1980-1985
Atlantic	<1	42	1983-1984
o,p'-DDT			
Pacific	<5	70	Prior to 1980
Western	<1-4	1352	1980-1985
Central	0.4-12	313	1980-1985
Atlantic	<1	42	1983-1984

[1] Detection limit is 1 $ng \cdot L^{-1}$.

Source: NAQUADAT 1985.

Table 6-124. Maximum DDT Concentrations in Various Species, Including Humans

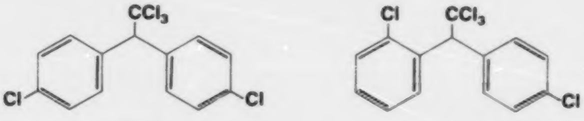
Species/ tissue type	DDT concentrations in tissue ($\mu g \cdot g^{-1}$ unless otherwise specified)	Reference
Lake Michigan coho salmon	19	Keller 1970
Fish (visceral fat)	24.9	Warner and Fenderson 1962
Cod liver oil	300 $mg \cdot L^{-1}$	Waldbott 1978
American egret (whole)	138	Rudd 1964
Western grebe (fat)	348	″
Double-crested cormorant (developing eggs)	20	″
Human fat (Germany)	2.3	West 1966; Keller 1970
Human fat (India)	26	″
Human fat (Canada)	4.9	West 1966
Human fat (U.S.A.)	12 (800 samples taken)	″
Occupational exposure of workers to DDT	1000	″
Human milk	0.13 $mg \cdot L^{-1}$	Laug *et al.* 1950; West 1964

Table 6-125. Environmental Concentration Ranges for *p,p'*-DDE in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	1-5	457	Prior to 1980
Western	<1-2	1496	1980-1984
Central	0.4-4	413	1980-1982
Atlantic	<1-2	52	1980-1984

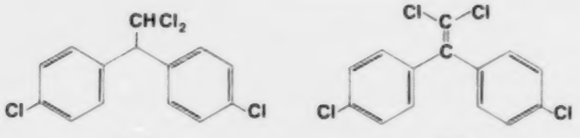
[1] Detection limit is 1 $ng \cdot L^{-1}$.

Source: NAQUADAT 1985.



p,p'-DDT o,p'-DDT

Figure 6-16. *p,p'*- and *o,p'*-DDT.



DDD DDE

Figure 6-17. DDD and DDE.

difficult to predict for aquatic systems, as most studies have not fully examined the variabilities of natural waters. Studies have shown that the volatilization of DDT from water is a rapid process. Although no useful data are available for quantitatively evaluating the rate of volatilization in specific aquatic systems, it has been estimated that DDT may be volatilized from water with a half-life of less than 1 week (U.S. EPA 1979).

DDT may be readily sorbed to suspended sediments and bottom muds. Soil partition coefficients of 10^3-10^7 have been found for some soils suspended in aqueous solutions; sorption increases with increasing soil organic content (U.S. EPA 1979). Some investigations have found that the amount of DDT taken up by clays is greater than the uptake of certain other chlorinated hydrocarbons (e.g. dieldrin and heptachlor) (Huang and Liao 1970).

Because of the persistent nature of DDT, coupled with its hydrophobic properties and solubility in lipids, this pesticide is concentrated by aquatic organisms at all trophic levels. It enters the food web, and is biomagnified (U.S. EPA 1980). Bioconcentration factors for DDT as high as 10^6 have been reported for several species in aquatic systems (U.S. EPA 1979). Biological half-lives have been found to range from 30 d for goldfish (*Carassius auratus*) (Grzenda *et al.* 1970), to 60 d for Atlantic salmon (*Salmo salar*) (Addison *et al.* 1976), to 160 d for rainbow trout (*Salmo gairdneri*) (Macek *et al.* 1970), to more than 1 year for brook trout (*Salvelinus fontinalis*) (Zinck and Addison 1975).

6.3.12.4.4.5 References

Addison, R.F., M.E. Zinck and J.R. Leahy. 1976. Metabolism of single and combined doses of ^{14}C-aldrin and ^{3}H-*p,p'*-DDT by Atlantic salmon (*Salmo salar*) fry. J. Fish. Res. Board Can. 33: 2073-2076.

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Grzenda, A.R., D.F. Paris and W.J. Taylor. 1970. The uptake, metabolism and elimination of chlorinated residues in goldfish (*Carassius auratus*) fed a ^{14}C-DDT diet. Trans. Am. Fish. Soc. 99: 385-396.

Health and Welfare Canada. 1980. Pesticides. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 457-470.

Huang, J.-C. and C.-S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 96(SA5): 1057-1078. (Cited in U.S. EPA 1979.)

Keller, E. 1970. The DDT story. Chemistry 43: 8-12.

Laug, E.P., C.S. Prickett and F.M. Kunze. 1950. Survey analyses of human milk and fat for DDT content. Fed. Proc. 9: 294-295. (Cited in Rudd 1964.)

Macek, K.J., C.R. Rodges, D.L. Stalling and S. Korn. 1970. The uptake, distribution and elimination of dietary ^{14}C-DDT and ^{14}C-dieldrin in rainbow trout. Trans. Am. Fish. Soc. 99: 689-695.

Marth, E.H. 1965. Residues and some effects of chlorinated hydrocarbon insecticides in biological material. Residue Rev. 9: 1-89.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

McNeil, E.E., R. Otson, W.F. Miles and F.J.M. Rajabalee. 1977. Determination of chlorinated pesticides in potable water. J. Chromatogr. 132: 277-286.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rudd, R.L. 1964. Pesticides in the Living Landscape. The University of Wisconsin Press, Madison, Wisconsin. 320 pp.

Singmaster, J.A., III. 1975. Environmental Behavior of Hydrophobic Pollutants in Aqueous Solutions. Ph.D. Thesis. Univ. California, Davis, California. University Microfilms, Ann Arbor, Michigan. Order No. 76-14,237. (Diss. Abstr. Int. B 1976, 36(12, pt. 1): 6206-6207.) (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. DDT. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/4-79-029a. pp. 25-1 to 25-22.

U.S. EPA. 1980. Ambient Water Quality Criteria for DDT. Office of Water Regulations and Standards Criteria, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-038.

Waldbott, G.L. 1978. Health Effects of Environmental Pollutants. The C.V. Mosby Co., St. Louis, Missouri. 350 pp.

Warner, K. and O.C. Fenderson. 1962. Effects of DDT spraying for forest insects on Maine trout streams. J. Wildl. Manage. 26: 86. (Cited in Marth 1965.)

West, I. 1964. Pesticides as contaminants. Arch. Environ. Health 9: 626-633. (Cited in West 1966.)

West, I. 1966. Biological effects of pesticides in the environment. *In* Organic Pesticides in the Environment. R.F. Gould (ed.). Adv. Chem. Ser. No. 60. pp. 38-53.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

Yule, W.N. and A.D. Tomlin. 1970. DDT in forest streams. Bull. Environ. Contam. Toxicol. 5: 479-488. (Cited in Health and Welfare Canada 1980.)

Zepp, R.G., N.L. Wolfe, J.A. Gordon and R.C. Fincher. 1976. Light-induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24: 727-733. (Cited in U.S. EPA 1979.)

Zinck, M.E. and R.F. Addison. 1975. The effect of temperature on the rate of conversion of *p,p'*-DDT to *p,p'*-DDE in brook trout (*Salvelinus fontinalis*). Can. J. Biochem. 53: 636-639.

6.3.12.4.5 Dieldrin

6.3.12.4.5.1 Uses and Production

Dieldrin has been one of the most widely used domestic pesticides (Lykken 1971; Waldbott 1978; U.S. EPA 1980). The original uses of dieldrin were as a pesticide for control of soil, fruit and vegetable pests, as well as for control of grasshoppers, locusts and termites. Its use was restricted in the U.S.A. in 1974 to those situations in which there is no effluent discharge (U.S. EPA 1980). In addition to being used as an insecticide, dieldrin has been used to treat woolen garments as a mothproofing agent (Marth 1965).

Table 6-126. Environmental Concentration Ranges for Dieldrin in Canadian Surface Waters

Region	Concentration range ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	<2-5	458	Prior to 1980
Western	<2	1352	1980-1981
Central	<4-5	316	1980-1981
Atlantic	<1-5	42	1980-1984

Source: NAQUADAT 1985.

The U.S.A. no longer manufactures dieldrin as a result of a ban in 1974, but instead imports the insecticide from the Shell Chemical Company which manufactures it in Holland (U.S. EPA 1980).

Dieldrin is not manufactured in Canada. No imports have been reported by the Shell Chemical Company of Canada, the registered supplier, in recent years (1980-1983) (Statistics Canada 1983, 1984; Agriculture Canada 1984).

Additional names for dieldrin include HEOD; Compound 497; Octalox; Insecticide no. 497; ENT 16225; Alvit; Dieldrex; Dieldrite; and Panoram D31 (U.S. EPA 1979; McNeely *et al.* 1979; Windholtz *et al.* 1983; Agriculture Canada 1984).

6.3.12.4.5.2 Sources and Pathways for Entering the Aquatic Environment

Dieldrin enters the environment through manufacturing emissions and application. Aldrin, another widely used chlorinated hydrocarbon insecticide, is rapidly metabolized to dieldrin (see Section 6.3.12.4.1) (U.S. EPA 1980).

The pathways for general environmental contamination by dieldrin include atmospheric dispersion, wind and water erosion of soil and transport while sorbed onto soil particles in the silt of streams, estuaries and oceans. Dieldrin can also move through the environment as residues in plants and animals, especially in fish and wildfowl (Lykken 1971).

6.3.12.4.5.3 Environmental Concentrations

Information concerning the environmental concentration ranges of dieldrin is sparse. Dieldrin was used in the late 1950's as a spray in an attempt to control the spread of fire ants in the southeastern United States. In 1957, 2.24 kg of dieldrin or heptachlor were sprayed per hectare. More than 1×10^6 ha were aerially treated (Rudd 1964).

Environmental concentration ranges for dieldrin taken from various regions across Canada are presented in Table 6-126. Dieldrin concentrations reported for Canadian drinking water in 1972 ranged from 0.05 to 5 $ng \cdot L^{-1}$ (NAQUADAT 1972; McNeil *et al.* 1977). In 1976, monthly samples taken of Ottawa drinking water had a concentration range for dieldrin of 0.1-4 $ng \cdot L^{-1}$ (1 $ng \cdot L^{-1}$ mean) (Williams *et al.* 1978).

6.3.12.4.5.4 Forms and Fate in the Aquatic Environment

Dieldrin, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,-7,8,8a-octahydro-*endo*-1,4-*exo*-5,8-dimethanonaphthalene

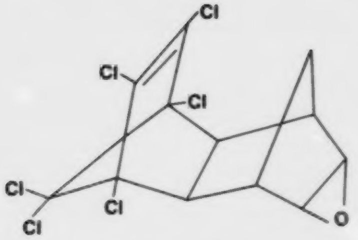


Figure 6-18. Dieldrin.

(Figure 6-18) is the epoxide of aldrin. It has a melting point of 175-176°C, a low vapour pressure (400 μPa at 20°C) (Worthing 1983) and a low water solubility (0.186 mg·L^{-1} at 20°C) (Park and Bruce 1968).

Dieldrin is considered to be persistent in the environment; sorption, volatilization and bioaccumulation are the important processes determining its fate (U.S. EPA 1979).

The hydrolysis of dieldrin in the aquatic environment is very slow (Eichelberger and Lichtenberg 1971). However, sorption to sediments containing organic matter is appreciable. An organic carbon partition coefficient (K_{oc}) of approximately 10^4 at 15°C has been reported (Weil *et al.* 1973).

Experimental studies suggest that direct photolysis of dieldrin does occur; its photolytic half-life is approximately 2 months (Henderson and Crosby 1968). Volatilization of dieldrin from aquatic systems is also an important removal process; half-lives in the order of a few hours to a few days have been determined from laboratory experiments (Singmaster 1975).

Dieldrin may be bioaccumulated by various organisms in the aquatic environment. Bioconcentration factors ranging from 10^2 to 10^4 for bacteria (Grimes and Morrison 1975) and averaging 10^4 for freshwater algae (Neudorf and Khan 1975) have been reported. Data from microcosm experiments also suggest significant bioaccumulation (Sanborn and Yu 1973; Metcalf *et al.* 1973), with bioconcentration factors in the order of 10^2-10^3 for algae, 10^4-10^5 for snails and 10^3 for fish. Biological half-lives in fish vary from 7 d in bluegill sunfish (*Lepomis macrochirus*) (Gakstatter and Weiss 1967) to 40 d in rainbow trout (*Salmo gairdneri*) (Macek *et al.* 1970). Very little microbial biotransformation of dieldrin occurs in the aquatic environment (Bohonos and Francis 1975; Sanborn *et al.* 1977).

6.3.12.4.5.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Bohonos, N. and A.J. Francis. 1975. Microbiological degradation of military standard pesticide formulations. Final Report. SRI to the U.S. Army Medical Research Development Command. Contract No. DADA17-73-C-3124. (Cited in U.S. EPA 1979.)

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Gakstatter, J.H. and C.M. Weiss. 1967. The elimination of ^{14}C-DDT and ^{14}C-dieldrin from fish following a single sublethal exposure in aquaria. Trans. Am. Fish. Soc. 96: 201-207.

Grimes, D.J. and Morrison, S.M. 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems. Microb. Ecol. 2: 43-59.

Henderson, G.L. and D.G. Crosby. 1968. The photodecomposition of dieldrin residues in water. Bull. Environ. Contam. Toxicol. 3: 131-134.

Lykken, L. 1971. Chemical control of pests. Chemistry 44: 18-21.

Macek, K.J., C.R. Rodgers, D.L. Stalling and S. Korn. 1970. The uptake, distribution and elimination of dietary ^{14}C-DDT and ^{14}C-dieldrin in rainbow trout. Trans. Am. Fish. Soc. 99: 689-695.

Marth, E.H. 1965. Residues and some effects of chlorinated hydrocarbon insecticides in biological material. Residue Rev. 9: 1-89.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

McNeil, E.E., R. Otson, W.F. Miles and F.J.M. Rajabalee. 1977. Determination of chlorinated pesticides in potable water. J. Chromatogr. 132: 277-286.

Metcalf, R.L., I.P. Kapoor, P.-Y. Lu, C.K. Schuth and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4: 35-44.

NAQUADAT. 1972. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Neudorf, S. and M.A.Q. Khan. 1975. Pickup and metabolism of DDT, dieldrin and photoaldrin by a freshwater alga (*Ankistrodesmus amalloides*) and a microcrustacean (*Daphnia pulex*). Bull. Environ. Contam. Toxicol. 13: 443-450.

Park, K.J. and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor epoxide. J. Econ. Entomol. 61: 770-[illegible]4.

Rudd, R.L. 1964. Pesticides and the Living Landscape. The University of Wisconsin Press, Madison, Wisconsin. 320 pp.

Sanborn, J.R. and C. Yu. 1973. The fate of dieldrin in a model ecosystem. Bull. Environ. Contam. Toxicol. 10: 340-346.

Sanborn, J.R., B.M. Francis, and R.L. Metcalf. 1977. The Degradation of Selected Pesticides in Soil: A Review of Published Literature. U.S. Environmental Protection Agency, Washington, D.C. EPA/600/9-77/022. (Cited in U.S. EPA 1979.)

Singmaster, J.A., III. 1975. Environmental Behavior of Hydrophobic Pollutants in Aqueous Solutions. Ph.D. Thesis. Univ. California, Davis, California. University Microfilms, Ann Arbor, Michigan. Order No. 76-14, 237. (Diss. Abstr. Int. B 1976, 36 (12, pt. 1): 6206-6207.) (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. Dieldrin. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 26-1 to 26-12.

U.S. EPA. 1980. Ambient Water Quality Criteria for Aldrin/Dieldrin. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-019.

Waldbott, G.L. 1978. Health Effects of Environmental Pollutants. The C.V. Mosby Co., St. Louis, Missouri. 316 pp.

Weil, L., G. Dure and K.E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6: 107-112.

Williams, D.T., F. Benoit, E. McNeil and R. Otson. 1978. Organochlorine pesticide levels in Ottawa drinking water, 1976. Pestic. Monit. J. 12: 163.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

Worthing, C.R. 1983. The Pesticide Manual. A World Compendium. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 191.

6.3.12.4.6 Endosulfan

6.3.12.4.6.1 Uses and Production

Endosulfan is used as a broad-spectrum insecticide and acaricide. In Canada, there are no restricted products containing endosulfan; however, 11 products are registered for domestic (home) use and commercial (industrial and agricultural) use. Endosulfan is used in Canada for the control of wood borers and other insects on fruit and ornamental trees and shrubs. Endosulfan is also registered to control insects on alfalfa, clover, corn, melons, potatoes, sunflowers, strawberries, certain fruit trees and tobacco (Agriculture Canada 1985).

Both technical-grade and formulated endosulfan are imported into Canada, but the actual amounts are too small to be reported in a separate category by Statistics Canada (Statistics Canada 1983, 1984).

An additional name for endosulfan used in Canada is Thiodan (Agriculture Canada 1984).

6.3.12.4.6.2 Sources and Pathways for Entering the Aquatic Environment

Endosulfan is applied to agricultural areas by aerial and ground spray techniques. Movement to aquatic environments is primarily via spray drift, leaching from soils and indirect transport, although several incidences of accidental contamination have been reported (Osmond 1969; NRCC 1975).

In 1979 and 1980 surveys of contaminants in treated water at treatment plant intakes in three cities along the Niagara River, α-endosulfan (Thiodan I) was detected in 1 of 29 samples at concentrations ranging from not detectable to 4 ng·L^{-1}. β-Endosulfan (Thiodan II), however, was not detected in any of the 29 samples analyzed in the same survey (Environment Canada/Ontario Ministry of the Environment 1981). In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 μg·L^{-1}) of α-endosulfan, β-endosulfan or endosulfan sulphate were observed in 15 samples (Environment Canada 1984).

6.3.12.4.6.3 Environmental Concentrations

Worldwide reports of endosulfan residues in the aquatic environment are extensive because of its widespread use on crops and occasional accidental spillage. In Canada, endosulfan is detectable in river samples in only about 10% of all samples analyzed for the chemical (detection limit 5 ng·L^{-1}). Endosulfan concentrations ranged from 20 to 83 ng·L^{-1} (Miles and Harris 1973; NRCC 1975), with one exceptionally high value of 260 ng·L^{-1} associated with a fish kill (Osmond 1969). Great Lakes water samples also showed about 10% incidence of detectable residues, with a range of 5-51 ng·L^{-1} (Environment Canada 1973).

Environmental concentration ranges for endosulfan in Canadian surface waters are presented in Table 6-127.

Table 6-127. Environmental Concentration Ranges for Endosulfan Isomers in Canadian Surface Waters

Region	Concentration range[1] (ng·L^{-1})	Number of samples	Sampling year(s)
α-Endosulfan			
Pacific	ND[2]-10	457	Prior to 1980
Western	ND	1352	1980-1985
Central	ND-10	300	1980-1985
Atlantic	ND-260	42	1980-1985
β-Endosulfan			
Pacific	<3-10	454	Prior to 1980
Western	<3	1352	1980-1985
Central	ND-10	300	1980-1985
Atlantic	ND-10	41	1980-1985

[1] Detection limit is 5 ng·L^{-1}.
[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-128. Concentration Ranges of α-Endosulfan (Thiodan I) in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water in 1979 and 1980

Location	Year	Total number of samples	Number of samples with detectable concentrations	Concentration range (ng·L^{-1})
Niagara-on-the-Lake	1979	7	1	ND[1]-3
	1980	12	0	ND
Niagara Falls	1979	7	1	ND-2
	1980	11	0	ND
Fort Erie	1979	7	0	ND
	1980	11	0	ND
St. Catharines	1980	5	0	ND

[1] ND = not detected; detection limit is 1 ng·L^{-1}.

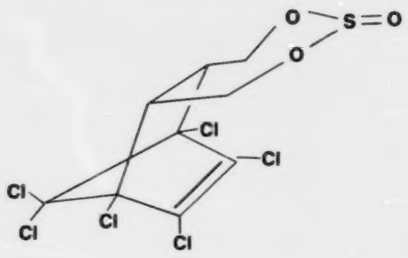
Source: Environment Canada/Ontario Ministry of the Environment 1981.

Concentration ranges of α-endosulfan (Thiodan I) in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-128. β-Endosulfan was not detected in any of the 60 samples taken in the same years (Environment Canada/Ontario Ministry of the Environment 1981).

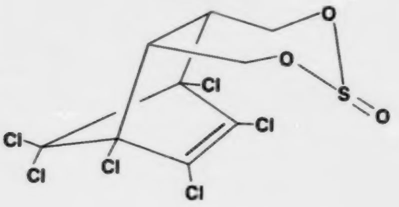
6.3.12.4.6.4 Forms and Fate in the Aquatic Environment

Endosulfan, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxanthiepin-3-oxide, exists in two isomeric forms, α- and β-isomers (Figure 6-19). Technical-grade endosulfan has a purity of 95%, and is usually composed of 70 and 30% α- and β-isomers, respectively (Berg 1976). The major transformations of endosulfan are oxidation to endosulfan sulphate (Figure 6-20) and hydrolysis (Berg 1976; U.S. EPA 1979).

The vapour pressure of endosulfan (isomer unspecified) is 1.3 mPa at 25°C (Martens 1972). Water solubility and octanol/water partition coefficients vary according to the specific isomer. For example, the water solubilities at 22°C and pH 7.2 for the α- and β-isomers and the sulphate are 0.15, 0.06 and



α-Endosulfan



β-Endosulfan

Figure 6-19. α- and β-Endosulfan.

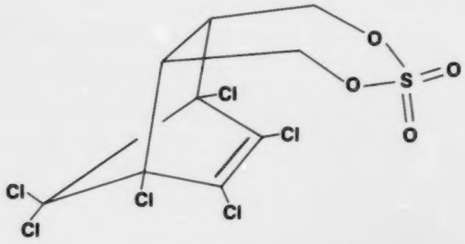


Figure 6-20. Endosulfan sulphate.

0.22 mg·L^{-1}, respectively (Braun and Frank 1973). Solubility increases slightly at lower pH (NRCC 1975). Calculated log octanol/water partition coefficients are 3.55, 3.62 and 3.66 for the α- and β-isomers and the sulphate, respectively (Ali 1978).

Although data are inconclusive, it appears that hydrolysis, photolysis, volatilization, sorption and bioaccumulation may all contribute to the environmental dynamics of endosulfan in the aquatic environment (U.S. EPA 1979).

Endosulfan will slowly hydrolyze in aqueous systems below pH 7 and at 20°C with a half-life of more than 1 month (U.S. EPA 1979). The α- and β-isomers were 82 and 87% recovered after 33 d in water used in a microcosm study (Ali 1978). Alternatively, at the end of 2 weeks in a sample of raw river water at pH 7.3-8.0, only 5% of the endosulfan remained (Eichelberger and Lichtenberg 1971), although some biotransformation may have taken place in this study. It has been shown that endosulfan sulphate is relatively resistant to hydrolysis in the aquatic environment (Ali 1978).

Sorption appears to be a relatively important removal process. Field studies have shown that more than 75% of the endosulfan measured in aquatic systems was associated with particulate matter, especially silt and mud (Greve and Wit 1971). Sorption appears to be proportional to the organic content of sediment (Richardson and Epstein 1971).

Endosulfan does photolyze in the solid and gaseous state and in nonaqueous solvents, usually with the production of endosulfan sulphate (U.S. EPA 1979). Endosulfan diol was found when an emulsion of either α- or β-endosulfan was irradiated in laboratory studies (Midwest Research Institute 1977). The limited information on photolysis does not permit the quantitative assessment of this process in the aquatic environment, although it does appear that endosulfan sulphate is more stable to photolysis than is endosulfan (U.S. EPA 1979).

In air-saturated water, endosulfan may be oxidized to endosulfan sulphate. Oxidation is independent of pH in the range of pH 5.5-7.2, and a half-life of approximately 70 d at 20°C has been predicted (Greve and Wit 1971). Theoretical calculations predict that endosulfan will be volatilized with a calculated half-life of 11 d (Mackay and Leinonen 1975). However, volatilization appears to be significantly reduced in the presence of particulate matter, indicating that sorption processes dominate distribution (Richardson and Epstein 1971).

Very little information is available on the bioaccumulation of endosulfan in the aquatic environment. α-Endosulfan was found to accumulate in saltwater mussels, with a wet weight bioconcentration factor in the order of 10^2 (Ernst 1977). Bioconcentration factors in a terrestrial-aquatic microcosm study were found to range from approximately 10-10^2 for fish, 10^2-10^3 for algae and mosquito larvae and 10^3-10^4 for snails (Ali 1978). The accumulation of endosulfan by aquatic organisms appears to be transitory, in that it is rapidly eliminated once the source of exposure has been removed. For example, the half-life of endosulfan (1 μg·L^{-1}) in goldfish (*Carassius auratus*) was estimated to be 3 d (NRCC 1975).

Endosulfan may be transformed in the presence of certain microorganisms (e.g. *Pseudomonas*) in water above pH 7 at 20°C with a high dissolved oxygen content. A half-life of approximately 1 week has been estimated (Greve and Wit 1971). The major product was endosulfan sulphate; however, it is not clear if the production of this oxidation product was biologically or chemically mediated (Greve and Wit 1971; U.S. EPA 1979).

6.3.12.4.6.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Ali, S. 1978. Degradation and Environmental Fate of Endosulfan Isomers and Endosulfan Sulfate in Mouse, Insect and Laboratory Model Ecosystem. Ph.D. Thesis. Univ. Illinois. Univ. Microfilms, Ann Arbor, Michigan. No. 78-20891. (Diss. Abstr. Int. B 1978, 39(5): 2117.) (Cited in U.S. EPA 1979.)

Berg, H. 1976. Farm Chemicals Handbook. Meister Publ. Co., Willoughby, Ohio.

Braun, H.E. and R. Frank. 1973. Unpublished data. Ontario Ministry of Agriculture and Food, Guelph, Ontario. (Cited in NRCC 1975.)

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Environment Canada. 1973. Pesticides Survey in Lakes Erie and Ontario, October 1973. For the Interdepartmental Working Group on Pesticide Research in the Great Lakes. Environmental Quality Coordination Unit, Canadian Centre for Inland Waters, Burlington, Ontario. 27 pp. (Cited in U.S. EPA 1980.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms – a steady state approach. Chemosphere 6: 731-740.

Greve, P.A. and S.L. Wit. 1971. Endosulfan in the Rhine River. J. Water Pollut. Control Fed. 43: 2338-2348.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Martens, R. 1972. Decomposition of endosulfan by soil microorganisms. Schriftenr. Ver. Wasser. Boden. Lufthyg. Berlin-Dahlem 37: 167-173. (Cited in U.S. EPA 1979.)

Midwest Research Institute. 1977. Initial Scientific Review of Endosulfan. MRI Report. November. (Cited in U.S. EPA 1979.)

Miles, J.R.W. and C.R. Harris. 1973. Organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas of Ontario, Canada, 1971. Pestic. Monit. J. 6: 363. (Cited in U.S. EPA 1980.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1975. Endosulfan. Its Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14098. 100 pp.

Osmond, D.S. 1969. A fish kill in the Thames River, Ontario. Ontario Ministry of the Environment, London, Ontario. Unpublished report. (Cited in NRCC 1975.)

Richardson, E.M. and E. Epstein. 1971. Retention of three insecticides on different size soil particles suspended in water. Soil Sci. Soc. Am. Proc. 35: 884-887. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. Endosulfan and endosulfan sulfate. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 27-1 to 27-16.

U.S. EPA. 1980. Ambient Water Quality Criteria for Endosulfan. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-046.

6.3.12.4.7 Endrin

6.3.12.4.7.1 Uses and Production

Endrin is a foliar insecticide used on cotton, corn, sugarcane, upland rice and many other crops (Worthing 1983). Endrin is registered with only one company in Canada; this company markets only one product, which has restricted use application. Endrin is registered in Canada for the control of certain insects in barley, flax, mustard, oats, potatoes, rape and wheat (Agriculture Canada 1985). Available importation data indicate that endrin has not been imported into Canada in recent years (1981-1983) (Statistics Canada 1983, 1984).

Additional names for endrin that are used in Canada include Endrex and Hexadrin (Agriculture Canada 1984).

6.3.12.4.7.2 Sources and Pathways for Entering the Aquatic Environment

The presence of endrin in the aquatic environment is related to either the manufacturing process or its application as a pesticide. Thus, endrin can reach the aquatic environment through drift from aerial spraying, surface runoff, percolation and subsurface runoff from treated lands, careless application or spillage, sewage discharge and industrial effluents (McNeely *et al.* 1979). In 1979 and 1980 surveys of contaminants in treated water at treatment plant intakes in three cities along the Niagara River, endrin was detected in 2 of 29 samples at concentrations ranging from not detectable (detection limit 1 $ng \cdot L^{-1}$) to 20 $ng \cdot L^{-1}$ (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.12.4.7.3 Environmental Concentrations

Environmental concentration ranges for endrin in Canadian surface waters are presented in Table 6-129. Concentration ranges of endrin in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-130.

6.3.12.4.7.4 Forms and Fate in the Aquatic Environment

Endrin, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*exo*-1,4-*exo*-5,8-dimethanonaphthalene (Figure 6-21), has a vapour pressure of 27 μPa at 25°C (Martin 1972), a water solubility of 0.26 $mg \cdot L^{-1}$ (Weil *et al.* 1974) and a calculated octanol/water partition coefficient of 5.6 (Neely *et al.* 1974).

Very little information is available on the fate of endrin in the aquatic environment. Hydrolysis does not appear to be important; 100% of the endrin was recovered from a sample of raw river water after 8 weeks (Eichelberger and Lichtenberg 1971). No information is available on sorption or volatilization of endrin in the aquatic environment (U.S. EPA 1979).

Photolysis of endrin in the solid state and in nonaqueous solutions has been reported (Fujita *et al.* 1969; Burton and Pollard 1974). However, no studies relevant to aquatic systems are available (U.S. EPA 1979).

Bioaccumulation appears to be an important fate for endrin in the aquatic environment; bioconcentration factors of 10^3-10^4 for aquatic species have been reported for microcosm studies (Metcalf *et al.* 1973). Steady-state bioconcentration factors have been measured for several freshwater organisms, including algae (122-140), mussels (3000) and fish (1640-15 000) (U.S. EPA 1980). Biological half-lives are, however, relatively short compared with those of chlorinated pesticides, such as DDT, with values of 1-2 weeks being reported (Jackson 1976).

Endrin has been found to undergo biotransformation in microbial isolate studies and microcosm studies. Twenty-five microbial isolates from soil showed activity in transforming endrin in solution, with γ-keto endrin being the major product, at yields of 5-95% (Matsumura *et al.* 1971). Endrin was biotransformed (23%) in the terrestrial phase of a terrestrial-aquatic microcosm (Metcalf *et al.* 1973). Anaerobic sewage sludge also transformed endrin; 50% of the endrin reacted in 5-14 d (Hill and McCarty 1967).

Table 6-129. Environmental Concentration Ranges for Endrin in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[2]-10	118	Prior to 1980
Western	ND	1352	1980-1985
Central	ND-10	310	1980-1985
Atlantic	<10	42	1980-1985

[1] Detection limit is 1 $ng \cdot L^{-1}$.
[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-130. Concentration Ranges of Endrin in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water in 1979 and 1980

Location	Year	Total number of samples	Number of samples with detectable concentrations	Concentration range ($ng \cdot L^{-1}$)
Niagara-on-the-Lake	1979	7	1	ND[1]-3
	1980	12	1	ND-9
Niagara Falls	1979	7	0	ND
	1980	11	2	ND-11
Fort Erie	1979	7	0	ND
	1980	11	0	ND
St. Catharines	1980	5	0	ND

[1] ND = not detected; detection limit is 1 $ng \cdot L^{-1}$.

Source: Environment Canada/Ontario Ministry of the Environment 1981.

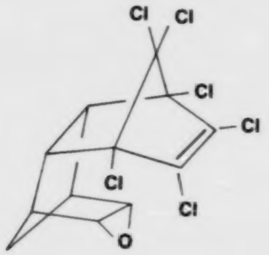


Figure 6-21. Endrin.

6.3.12.4.7.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Burton, W.B. and G.E. Pollard. 1974. Rate of photochemical isomerization of endrin in sunlight. Bull. Environ. Contam. Toxicol. 12: 113-116.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Fujita, M., A. Ishii and Y. Sakagami. 1969. Photodecomposition of endrin. J. Hyg. Chem. 15: 9-12. (Cited in U.S. EPA 1979.)

Hill, D.W. and P.L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39: 1259-1277.

Jackson, G.A. 1976. Biologic half-life of endrin in channel catfish tissues. Bull. Environ. Contam. Toxicol. 16: 505-507.

Martin, H. 1972. Pesticide Manual. 3rd edition. British Crop Protection Council, Worcester, England.

Matsumura, F., V.G. Khanvilkar, K.C. Patil and G.M. Boush. 1971. Metabolism of endrin by certain soil microorganisms. J. Agric. Food Chem. 19: 27-31.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

Metcalf, R.L., I.P. Kapoor, P.-Y. Lu, C.K. Schuth and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4: 35-44.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. Endrin and endrin aldehyde. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 28-1 to 28-11.

U.S. EPA. 1980. Ambient Water Quality Criteria for Endrin. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-047.

Weil, L., G. Dure and K.L. Quentin. 1974. Solubility in water of insecticide chlorinated hydrocarbons and polychlorinated biphenyls in view of water pollution. Z. Wasser Abwasser Forsch. 7: 169-175. (Cited in U.S. EPA 1979.)

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 235.

6.3.12.4.8 Heptachlor

6.3.12.4.8.1 Uses and Production

Heptachlor is used for the control of a variety of insects and insect larvae, including ants, cutworms, maggots, termites, thrips, weevils and wireworms. Heptachlor, which is a nonsystemic contact and stomach insecticide, is also used to control household insects and pests of man and domestic animals (Worthing 1983).

Only one company is authorized to market heptachlor in Canada. The product that is marketed is restricted in use application, and the British Columbia Ministry of the Environment requires a permit for the use of heptachlor in that province. In Canada, heptachlor is registered for use in the control of the narcissus bulb fly (Agriculture Canada 1985).

In 1981, 1982 and 1983, formulated heptachlor was imported into Canada in the amounts of 8, 2 and 1 t, respectively (Statistics Canada 1983, 1984).

6.3.12.4.8.2 Sources and Pathways for Entering the Aquatic Environment

The presence of heptachlor in the aquatic environment is directly related to either the manufacturing process or its application as a pesticide. Heptachlor can reach the aquatic environment through drift from aerial spraying, surface runoff, percolation and subsurface runoff from treated lands, careless application or spillage, sewage discharge and industrial effluents (McNeely *et al.* 1979).

In 1979 and 1980 surveys of contaminants in treated water at treatment plant intakes in three cities along the Niagara River, heptachlor was not detected (detection limit 1 ng·L^{-1}) in any of the 29 samples taken (Environment Canada 1984). In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 μg·L^{-1}) of heptachlor were observed in 15 samples (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.12.4.8.3 Environmental Concentrations

Concentrations of heptachlor in Canadian surface waters have been measured in several areas and regions. Environmental concentration ranges for heptachlor in Canadian surface waters are presented in Table 6-131. Heptachlor was not detected in any of the 60 samples taken of surface waters near four cities on the Niagara River in 1979 and 1980 surveys (Environment Canada 1984).

6.3.12.4.8.4 Forms and Fate in the Aquatic Environment

Heptachlor, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, has a water solubility of 0.056 mg·L^{-1} at 25-29°C (Park and Bruce 1968) and a vapour pressure of 0.04 Pa at 25°C (Martin 1972). The technical mixture contains approximately 71% heptachlor (Figure 6-22) and 29% related compounds (Ashworth *et al.* 1970).

Hydrolysis, sorption, bioaccumulation and biotransformation appear to be the major processes determining the fate of heptachlor in the aquatic environment (U.S. EPA 1979).

The predominant environmental process that determines the fate of heptachlor, with a half-life of about 1-3 d, is hydrolysis to 1-hydroxychlordene. 1-Hydroxychlordene is then transformed to 1-hydroxy-2,3-chlordene epoxide (U.S. EPA 1979). The half-life of heptachlor in unbuffered distilled water at 30°C was found to be 23 h. Complete removal of heptachlor, with the production of 1-hydroxychlordene, occurred within 2 weeks in a sample of river water held at room temperature (Eichelberger and Lichtenberg 1971).

Sorption appears to play a significant role in the aquatic fate of heptachlor. Sorption coefficients of 10^5-10^6 have been found for various clays, such as montmorillonite, illite, kaolinite and leonardite, and humic acids (Huang and Liao 1970; Huang 1971).

There is insufficient information to determine if photolysis is a significant process. Photolysis of heptachlor adsorbed on solid phases and dissolved in nonaqueous solvents has been demonstrated (U.S. EPA 1979). Although solid-state photolysis yields heptachlor epoxide (Ehmann 1976), the epoxide is not expected to be produced in any possible aqueous-phase photolytic reactions (U.S. EPA 1979). Current information is not sufficient to quantitatively determine the importance of volatilization of heptachlor from the aquatic environment. However, it may be significant because heptachlor has a relatively low vapour pressure compared with other cyclodiene insecticides (U.S. EPA 1979).

Table 6-131. Environmental Concentration Ranges for Heptachlor in Canadian Surface Waters

Region	Concentration range[1] (ng·L^{-1})	Number of samples	Sampling year(s)
Pacific	ND[2]-5	457	Prior to 1980
Western	ND	1496	1980-1985
Central	ND-3	315	1980-1985
Atlantic	ND	42	1980-1985

[1] Detection limit is 1 ng·L^{-1}.
[2] ND = not detected.

Source: NAQUADAT 1985.

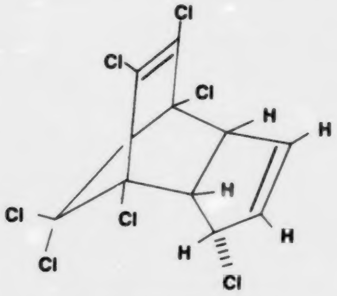


Figure 6-22. Heptachlor.

Heptachlor bioaccumulation has been reported for various aquatic organisms; bioconcentration factors are in the order of 10^4 (Lu *et al.* 1975). A biological half-life of approximately 28 d was found for ^{14}C-heptachlor injected into goldfish (*Carassius auratus*) (Feroz and Khan 1979). Reports indicate that biotransformation of heptachlor by oxidation leads to the formation of heptachlor epoxide; biotransformation by reduction results in the formation of chlordene. However, abiotic hydrolysis of heptachlor in solution is more rapid than biotransformation, with the hydrolysis product itself then being biologically epoxidized. Although detected in the aquatic environment, heptachlor epoxide does not appear to be a major product of heptachlor degradation in aquatic systems (see Section 6.3.12.4.9) (U.S. EPA 1979).

6.3.12.4.8.5 References

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Ashworth, R. de B., J. Henriet and J.F. Lovett. 1970. CIPAC Handbook. Vol. 1. Analysis of Technical and Formulated Pesticides. G.R. Raw (ed.). Collaborative International Pesticides Analytical Council Ltd., W. Heffer and Sons Ltd., Cambridge, England. 1079 pp.

Ehmann, J.L. 1976. A Model System: The Photochemical Interaction of Heptachlor and Selected Epicuticular Wax Components of the Tomato Fruit and Pear Leaf. Ph.D. Thesis, Michigan State University. University Microfilm, Ann Arbor, Michigan, No. 70-18, 615. (Diss. Abstr. Int. B 1976, 37(2): 597-598.) 102 pp. (Cited in U.S. EPA 1979.)

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Feroz, M. and M.A.Q. Khan. 1979. Metabolism of ^{14}C-heptachlor in goldfish (*Carassius auratus*). Arch. Environ. Contam. Toxicol. 8: 519-531.

Huang, J.-C. 1971. Effect of selected factors on pesticide sorption and desorption in the aquatic system. J. Water Pollut. Control Fed. 43: 1739-1748.

Huang, J.-C. and C.-S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 96(SAS): 1057-1078. (Cited in U.S. EPA 1979.)

Lu, P.-Y. R.L. Metcalf, A.S. Hirwe and J.W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordene, heptachlor and heptachlor epoxide in a laboratory model ecosystem. J. Agric. Food Chem. 23: 967-973.

Martin, H. 1972. Pesticide Manual. 3rd edition. British Crop Protection Council, Worcester, England. (Cited in U.S. EPA 1979.)

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Park, K.S. and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor epoxide. J. Econ. Entomol. 61: 770-774. (Cited in U.S. EPA 1979.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. Heptachlor. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 29-1 to 29-17.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 306.

6.3.12.4.9 Heptachlor Epoxide

6.3.12.4.9.1 Uses and Production

Heptachlor epoxide is used to control a variety of insects and insect larvae. In Canada, heptachlor epoxide is not registered for use as a pesticide (Agriculture Canada 1984). There are no available data on importation.

6.3.12.4.9.2 Sources and Pathways for Entering the Aquatic Environment

The presence of heptachlor epoxide in the aquatic environment is directly related to either the manufacturing process or its application as a pesticide. Heptachlor epoxide can reach the aquatic environment through drift from aerial spraying, surface runoff, percolation and subsurface runoff from treated lands, careless application or spillage, sewage discharge and industrial effluents (McNeely *et al.* 1979). Heptachlor epoxide may also be formed from the epoxidation of heptachlor (U.S. EPA 1979).

Table 6-132. Environmental Concentration Ranges for Heptachlor Epoxide in Canadian Surface Waters

Region	Concentration range[1] ($ng \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[2]-5	458	Prior to 1980
Western	ND	3704	1980-1985
Central	ND	327	1980-1985
Atlantic	ND	42	1980-1985

[1] Detection limit is 1 $ng \cdot L^{-1}$.

[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-133. Concentration Ranges of Heptachlor Epoxide in Surface Waters at Treatment Plant Intakes and in Upper Niagara River Water in 1979 and 1980

Location	Year	Total number of samples	Number of samples with detectable concentrations	Concentration range ($ng \cdot L^{-1}$)
Niagara-on-the-Lake	1979	7	1	ND[1]-10
	1980	12	1	ND-8
Niagara Falls	1979	7	0	ND
	1980	11	2	ND-2
Fort Erie	1979	7	0	ND
	1980	11	2	ND-14
St. Catharines	1980	5	0	ND

[1] ND = not detected; detection limit is 1 $ng \cdot L^{-1}$.

Source: Environment Canada/Ontario Ministry of the Environment 1981.

In a 1980-1981 survey of various contaminants in industrial effluent in the St. Lawrence River at Cornwall, Ontario, no detectable concentrations (detection limit 0.5 $\mu g \cdot L^{-1}$) of heptachlor epoxide were observed in 15 samples (Environment Canada 1984).

6.3.12.4.9.3 Environmental Concentrations

Concentrations of heptachlor epoxide in Canadian surface waters have been reported for several areas and regions. Environmental concentration ranges for heptachlor epoxide in Canadian surface waters are presented in Table 6-132. Concentration ranges of heptachlor epoxide in raw water at treatment plant intakes and in upper Niagara River water during 1979 and 1980 are presented in Table 6-133. Also in the 1979 and 1980 surveys, contaminants in treated water at treatment plant intakes in three cities along the Niagara River were sampled, and heptachlor epoxide was detected in 2 of 29 samples at a concentration of 1 $ng \cdot L^{-1}$ (the detection limit) (Environment Canada/Ontario Ministry of the Environment 1981).

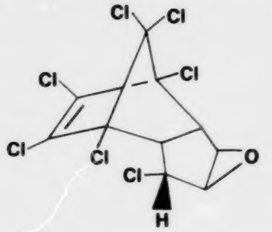


Figure 6-23. Heptachlor epoxide.

6.3.12.4.9.4 Forms and Fate in the Aquatic Environment

Heptachlor epoxide, 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene, has a water solubility of 0.35 $mg \cdot L^{-1}$ (Park and Bruce 1968). It exists in two isomeric forms, with the structure shown in Figure 6-23 being the toxic and probably dominant isomer (Singh 1969).

Heptachlor epoxide is generally resistant to chemical and biological transformations in the aquatic environment, and has a predicted half-life of several years (U.S. EPA 1979).

Hydrolysis is not considered to be a significant removal process for heptachlor epoxide; heptachlor epoxide solutions remained relatively unchanged after 3 weeks in samples of river water held at pH 7.3-8 and room temperature (Eichelberger and Lichtenberg 1971). Although photolysis does occur in the solid phase and in nonaqueous solutions, it is not expected to be an important process in aquatic systems. No information is available on volatilization (U.S. EPA 1979), although heptachlor epoxide has been found in rain samples (Strachan 1985).

Sorption of heptachlor epoxide does not appear to be extensive. Sorption coefficients ranging from approximately 200 to 700 have been recorded for humic acids, soils and clay (Hill and McCarty 1967; Weil *et al*. 1973).

Bioconcentration factors of 60-15 200 have been found for heptachlor epoxide in several bacteria (Grimes and Morrison 1975). In terrestrial-aquatic microcosm studies, bioconcentration factors of 10^3-10^4 were recorded (Park and Bruce 1968). Heptachlor epoxide had a biological half-life in goldfish (*Carassius auratus*) of more than 28 d (Feroz and Khan 1979).

Heptachlor epoxide was found to be resistant to biotransformation in microcosm studies (Lu *et al*. 1975), and was slowly degraded in anaerobic sewage sludge (50% loss in 60 d) (Hill and McCarty 1967). In the aquatic environment, biotransformation is probably a minor process, and it is likely that heptachlor epoxide will remain intact with a half-life approaching several years (U.S. EPA 1979).

6.3.12.4.9.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Feroz, M. and M.A.Q. Khan. 1979. Metabolism of ^{14}C-heptachlor in goldfish (*Carassius auratus*). Arch. Environ. Contam. Toxicol. 8: 519-531.

Grimes, D.J. and S.M. Morrison. 1975. Bacterial bioconcentration of chlorinated hydrocarbon insecticides from aqueous systems. Microb. Ecol. 2: 43-59. (Cited in U.S. EPA 1979.)

Hill, D.W. and P.L. McCarty. 1967. Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39: 1259-1277.

Lu, P.-Y., R.L. Metcalf, A.S. Hirwe and J.W. Williams. 1975. Evaluation of environmental distribution and fate of hexachlorocyclopentadiene, chlordane, heptachlor and heptachlor epoxide in a laboratory model ecosystem. J. Agric. Food Chem. 23: 967-973.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Pesticides. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 34-45.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Park, K.S. and W.N. Bruce. 1968. The determination of the water solubility of aldrin, dieldrin, heptachlor and heptachlor epoxide. J. Econ. Entomol. 61: 770-774. (Cited in U.S. EPA 1979.)

Singh, J. 1969. Conversion of heptachlor to its epoxide. Bull. Environ. Contam. Toxicol. 4: 77-79.

Strachan, W.M.J. 1985. Personal communication. Environmental Contaminants Division, National Water Research Institute, Environment Canada, Burlington, Ontario.

U.S. EPA. 1979. Heptachlor epoxide. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 30-1 to 30-9.

Weil, L., G. Dure and K.E. Quentin. 1973. Adsorption of chlorinated hydrocarbons to organic particles and soils. Z. Wasser Abwasser Forsch. 6: 107-112. (Cited in U.S. EPA 1979.)

6.3.12.4.10 Hexachlorocyclohexanes

6.3.12.4.10.1 Uses and Production

Benzene hexachloride (BHC) is the common name used to describe the mixed stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH). The γ-isomer, called lindane, is the only hexachlorocyclohexane isomer possessing significant insecticidal activity (NAS 1977; Gummer 1979; Fuchs and Schröder 1983).

BHC (technical grade) is a mixture of the eight possible isomers that constitute the different spatial arrangements of the six chlorine atoms on the *trans* form of the cyclohexane ring. Its composition approximates 65% α-isomer; 11% β; 13-14% γ; 8-9% δ; and 1% ϵ. The lowest melting point compound, melting at 112.8°C, is designated as the γ-isomer (Melnikov 1971a, b; NAS 1977). Because γ-BHC (lindane) is the active ingredient in technical-grade BHC (Hardie 1972), technical-grade BHC now has limited use commercially except as the raw material from which the purified γ-isomer is extracted (U.S. EPA 1980).

γ-BHC (lindane) has been used to control insects in domestic and commercial settings, in numerous agricultural and silvicultural applications and in dips, sprays and dusts for livestock and domestic pets (NAS 1975, 1977). Lindane is registered in Canada for controlling ticks and flies on livestock, seed treatment for wireworm control, controlling infestations of stored logs by the logging industry and controlling bedbugs by the pest control industry. Additional uses are on nursery stock trees, as soil treatment, in dog pounds for control of fleas, in farm buildings (wall spraying) and in warehouses where food is not stored (Gummer 1979).

No production of lindane occurs in Canada (Agriculture Canada 1984). Table 6-134 shows the importation into Canada of lindane as the formulated pesticide (marketed under the name Hexachlor) and contained in a mixture of hexachlorocyclohexane isomers (Statistics Canada 1983, 1984).

Additional names for lindane include gamma-BHC[*]; gamma-HCH[*]; gamma-BHC from lindane containing a minimum of 99%[*]; γ-Lindane; γ-Benzene Hexachloride[*]; Hexachlor; ENT7796; Aparasin; Aphtiria; Gammalin; Gamene; Gamiso; Gammexane[*]; Gexane; Jacutin; Kwell; Lindafor; Lindatox; Lorexane; Quellada; Streunex; Tri-6; Viton; 666; Lindamul; Nexit-Staub; and Prodactic (U.S. EPA 1979, 1980; Windholtz *et al.* 1983).

6.3.12.4.10.2 Sources and Pathways for Entering the Aquatic Environment

Direct and indirect application of lindane, agricultural runoff and industrial discharges are the principal sources of lindane in surface waters (Edwards 1973). Long-range transport and, consequently, atmospheric deposition appear to be the mechanisms by which lindane and its isomers occur in the surface waters of isolated areas of Canada (U.S. EPA 1979). Other sources include the pulp and paper industry, pesticide packaging and manufacturing plants, farm buildings and warehouse spraying and the seed dressing industry (Gummer 1979).

6.3.12.4.10.3 Environmental Concentrations

In a study of surface waters of western Canada between 1971 and 1977, about 58% of the stations sampled (149 of 258 stations) were found to have detectable concentrations (detection limit 1 $ng\cdot L^{-1}$) of lindane at one or more times during the monitoring period. Six of the water quality districts in western Canada recorded maximum concentrations at or above 5 $ng\cdot L^{-1}$. The highest value, 86 $ng\cdot L^{-1}$, was recorded in the Qu'Appelle River district (Gummer 1979).

Lindane was not as prevalent as α-BHC in the surface waters of western Canada, where α-BHC concentrations ranged from 1 to 20 $ng\cdot L^{-1}$. α-BHC was found in fish and wildlife in Alberta, with a concentration of 0.15-0.28 $mg\cdot kg^{-1}$ (Gummer 1979).

From 333 surface water sampling locations across Canada, lindane was detected in 748 of 3160 samples taken. Concentrations were found to range from <1 to 310 $ng\cdot L^{-1}$ (Environment Canada 1977). The highest concentration found in Canadian tap water was 5 $ng\cdot L^{-1}$ at Sherbrooke, P.E.I. (NAQUADAT 1977). Environmental concentration ranges for lindane and α-BHC in Canadian surface waters are presented in Table 6-135.

Table 6-134. Importation of Lindane and Mixed Hexachlorocyclohexane Isomers into Canada

	Amount (t)		
Compound	1981	1982	1983
Hexachlorocyclohexane (all isomers)	146	106	148
Hexachlor (formulated pesticide)	3	1	–

Sources: Statistics Canada 1983, 1984.

Table 6-135. Environmental Concentration Ranges for Lindane and α-BHC in Canadian Surface Waters

BHC isomer	Region	Concentration range[1] ($ng\cdot L^{-1}$)	Number of samples	Sampling year(s)
Lindane	Pacific	0.7-13	465	Prior to 1980
	Western	1-8	1351	1980-1981
	Central	0.4-7	325	1980-1983
	Atlantic	1-5	42	1980-1984
α-BHC	Pacific	1-6	119	Prior to 1980
	Western	1-20	1344	1980-1982
	Central	0.4-28	331	1980-1983
	Atlantic	1-10	66	1980-1984

[1] Detection limit is 1 $ng\cdot L^{-1}$.

Source: NAQUADAT 1985.

6.3.12.4.10.4 Forms and Fate in the Aquatic Environment

Lindane, the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (Figure 6-24), is considered to be the most important hexachlorocyclohexane stereoisomer for insecticidal application. It has a water solubility ranging from approximately 2 $mg\cdot L^{-1}$ at 15°C to 8 $mg\cdot L^{-1}$ at 25°C, and a vapour pressure ranging from 0.02-0.04 Pa (U.S. EPA 1979) to 1.9 Pa (Melnikov 1971a). The α-isomer of hexachlorocyclohexane (α-BHC) has a water solubility of 10 $mg\cdot L^{-1}$ and a vapour pressure of 8 Pa, whereas the β-isomer (β-BHC) has a water solubility of 5 $mg\cdot L^{-1}$ and a vapour pressure of 22.7 Pa (Melnikov 1971a).

Most studies indicate that lindane is relatively stable in the water column (U.S. EPA 1979, 1980). Sorption to suspended sediment and biota is not extensive, with the majority of lindane remaining in the water column for extended periods of time (Hamelick and Waybrant 1976). Although not a primary removal mechanism, sorption may ultimately transport lindane to sediments where transformation can occur (U.S. EPA 1979).

Because lindane has a saturated structure, it should have little or no ultraviolet absorption above 290 nm. Photolysis in aquatic systems is equivocal, and available information is insufficient to determine if it is an important removal mechanism (U.S. EPA 1979). Volatilization is believed to be a relatively minor removal process for lindane, as it has a calculated volatility half-life of 200 d (Mackay and Leinonen 1975).

Lindane can be biologically transformed, with half-lives in the order of several days to more than a year, when introduced into biologically active aquatic environments. Anaerobic processes in sediments appear to be more efficient than aerobic

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[*] Names registered for use in Canada (Statistics Canada 1983, 1984; Agriculture Canada 1984).

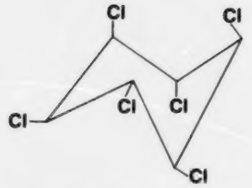


Figure 6-24. γ-Hexachlorocyclohexane (lindane).

processes, with the major products of biodegradation being penta- and tetrachlorocyclohexanes (U.S. EPA 1979).

Lindane may be bioaccumulated in aquatic organisms (calculated log octanol/water partition coefficient at 25°C is 3.72) (Kurihara *et al*. 1973). Although few reliable data are available, bioconcentration factors of less than 10^2 for aquatic invertebrates and 10^2 for fish have been reported (Metcalf *et al*. 1973; Sanborn 1974; Hamelick and Waybrant 1976; Kenaga 1980). Lindane appears to be rapidly eliminated once continuous exposure ceases. For example, a half-life of less than 2 d was found for lindane depuration by bluegill sunfish (*Lepomis macrochirus*) (Rodgers *et al*. 1983).

6.3.12.4.10.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Edwards, C.A. 1973. Persistent Pesticides in the Environment. CRC Press, Cleveland, Ohio. (Cited in Gummer 1979.)

Environment Canada. 1977. Surface Water Quality in Canada – An Overview. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Fuchs, R.A. and R. Schröder. 1983. Agents for control of animal pests. *In* Chemistry of Pesticides. K.H. Büchel (ed.). John Wiley & Sons, New York. pp. 9-226.

Gummer, W.D. 1979. Pesticide Monitoring in the Prairies of Western Canada. Water Quality Branch – Western and Northern Region, Inland Waters Directorate, Environment Canada, Regina, Saskatchewan. Water Quality Interpretive Rep. No. 4.

Hamelick, J.L. and R.C. Waybrant. 1976. DDE and lindane in a large-scale model lentic ecosystem. Trans. Am. Fish. Soc. 105: 124-134.

Hardie, D.W.F. (ed.). 1972. Kirk-Othmer Encyclopedia of Chemical Technology. Interscience Publ., Inc., New York. (Cited in U.S. EPA 1980.)

Kenaga, E.E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. Environ. Sci. Technol. 14: 553-556.

Kurihara, N., M. Uchida, T. Fujita and M. Nakajima. 1973. Studies on BHC isomers and related compounds. V. Some physiochemical properties of BHC isomers. Pestic. Biochem. Physiol. 2: 383-390.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Melnikov, N.N. 1971a. Halogen derivatives of alicyclic hydrocarbons. Residue Rev. 36: 42-66. (Cited in NAS 1977.)

Melnikov, N.N. 1971b. Chemistry of pesticides. Residue Rev. 36: 371-372. (Cited in NAS 1977.)

Metcalf, R.L., I.P. Kapoor, P.-Y. Lu, C.K. Schuth and P. Sherman. 1973. Model ecosystem studies of the chemical fate of six organochlorine pesticides. Environ. Health Perspect. 4: 35-44.

NAQUADAT. 1977. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1975. Pest Control: An Assessment of Present and Alternative Technologies. Vol. I. Contemporary Pest Control Practices and Prospects: The Report of the Executive Committee. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 506 pp. (Cited in NAS 1977.)

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences. U.S. National Research Council, Washington, D.C. 939 pp.

Rodgers, J.H., K.L. Dickson and M.J. DeFoer. 1983. Bioconcentration of lindane and naphthalene in bluegills (*Lepomis macrochirus*). *In* 6th Symp. Aquatic Toxicology and Hazard Assessment. W.E. Bishop, R.D. Cardwell and B.B. Heidolph (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. ASTM STP 802. pp. 300-311.

Sanborn, J.R. 1974. The Fate of Select Pesticides in the Aquatic Environment. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA-660/3-74-025. 83 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

U.S. EPA. 1979. γ-Hexachlorocyclohexane (lindane). *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 32-1 to 32-16.

U.S. EPA. 1980. Ambient Water Quality Criteria for Hexachlorocyclohexane. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-054.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

6.3.12.4.11 Methoxychlor

6.3.12.4.11.1 Uses and Production

Methoxychlor is used for the control of blackfly larvae in streams in northern and southern regions of Canada, the beetle vector of Dutch Elm disease and flies on farm animals. It is also used in homes and gardens, and is registered for use on virtually all fruits and vegetables and a variety of grains (NRCC 1975; NAS 1977).

In 1971, 1972 and 1973, 122, 80.1 and 32.2 t, respectively, of methoxychlor were sold in Canada (NRCC 1975). Recent sales of methoxychlor are not available. In 1981, 11 t of methoxychlor were imported into Canada. Formulated methoxychlor was imported into Canada in the amounts of 8 and 5 t in 1981 and 1982, respectively (Statistics Canada 1983). An additional name for methoxychlor used in Canada is Marlate (Agriculture Canada 1984).

6.3.12.4.11.2 Sources and Pathways for Entering the Aquatic Environment

Methoxychlor may enter the aquatic environment from direct application for fly control, spray drift from adjacent agricultural areas or runoff from sprayed areas. Methoxychlor has been found to adsorb strongly to the soils to which it is applied. This, in combination with its low water solubility, would indicate

Table 6-136. **Environmental Concentration Ranges for Methoxychlor in Canadian Surface Waters and Sediment**

Region	Concentration range (ng·L^{-1} or ng·g^{-1})	Number of samples	Sampling year(s)
Pacific			
Surface waters	<0.7[1]-12	458	Prior to 1980
Western			
Surface waters	<10[1]	1291	1980-1985
Central			
Surface waters	0.4[1]-10	303	1980-1985
Lake sediment	<50[2]	12	1982
Atlantic			
Surface waters	<10[1]	41	1980-1985
Lake/stream sediment	<50[2]	2	1980

[1] Detection limit is 10 ng·L^{-1}.

[2] Detection limit is 10 ng·kg^{-1}.

Source: NAQUADAT 1985

a strong tendency to remain in soil or the sediment of an aquatic system (NRCC 1975).

6.3.12.4.11.3 Environmental Concentrations

There are few reports of aquatic contamination by methoxychlor, most of which are related to direct application to the aquatic environment. The one report that dealt with indirect methoxychlor residues in water reported levels in the Lake Utah watershed as high as 5.2 µg·L^{-1} at the time of spray in adjacent areas (Bradshaw *et al.* 1972). Streams that had been purposely sprayed with methoxychlor had initially high concentrations in water and sediment (300 µg·L^{-1}) which rapidly (1-20 h) declined to nondetectable levels (Charnetski *et al.* 1980). Residues in fish in these streams showed a similar pattern (Lockhart *et al.* 1977). Environmental concentration ranges for methoxychlor in Canadian surface waters and sediment are presented in Table 6-136.

Methoxychlor is not detectable in Great Lakes water; however, fish and other organisms have been shown to contain trace amounts, whereas phytoplankton of Lake Erie and Lake Ontario can have very high levels (23-71 µg·kg^{-1}) (Environment Canada 1973). Methoxychlor has been found to be a major organic carbon constituent of rainfall in the Lake Superior area, at a mean concentration of 2.4 ng·L^{-1} (Strachan 1985).

6.3.12.4.11.4 Forms and Fate in the Aquatic Environment

Technical formulations of methoxychlor, 1,1,1-trichloro-2,2-bis (4-methoxyphenyl)-ethane, contain approximately 93% of the *p,p'*-isomer (Figure 6-25) (Lamoureux and Feil 1980). Methoxychlor has a low vapour pressure and a solubility in water of 0.26 mg·L^{-1} (Kapoor *et al.* 1970). However, there is little specific information available concerning the processes that determine its fate in the aquatic environment (NRCC 1975).

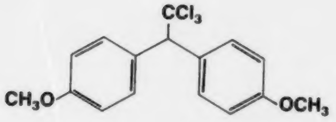


Figure 6-25. ***p,p'*-Methoxychlor.**

Hydrolysis does not appear to be significant; half-lives of approximately 1 year have been reported (Wolfe *et al.* 1977). Direct photolysis is also insignificant in aqueous solutions under normal sunlight intensity. Methoxychlor in distilled water is slowly photodegraded, with a half-life of approximately 12-13 d. Sunlight photolysis of methoxychlor in distilled water containing soluble organic matter, such as humic acid, proceeds at a faster rate; a half-life of approximately 7 h has been observed (Zepp *et al.* 1976). Hence, sensitizing photolytic processes may play a role in the removal of methoxychlor from the water column. Volatilization is not expected to be a significant removal process (NRCC 1975). However, the detection of methoxychlor in rainfall does indicate that some volatilization may be occurring (Strachan 1985).

Sorption to suspended and bed sediments is probably the major removal process of methoxychlor from the water column. Because methoxychlor has a high calculated octanol/water partition coefficient (~10^5) (Karickhoff 1980), it is expected that a major fraction of methoxychlor in the aquatic environment would be found adsorbed to organic material. Approximately 50% of the methoxychlor found in Saskatchewan River samples was associated with suspended sediments (Fredeen *et al.* 1975).

There is little evidence that microbial degradation plays a significant role in removal of methoxychlor from the aquatic environment. Under anaerobic conditions in a laboratory study, approximately 75% of methoxychlor was degraded in 5 d by *Aerobacter aerogenes*; however, under aerobic conditions, only 10% was degraded (Mendel *et al.* 1967). Methoxychlor is not readily metabolized by some invertebrates (primarily insects and molluscs) and plants in the aquatic environment, indicating a potential for bioaccumulation (Reinbold *et al.* 1971; NRCC 1975). High levels of methoxychlor were found in phytoplankton in the Great Lakes (Environment Canada 1973). However, low bioconcentration factors for higher organisms, including fish (Kenaga 1980), indicate a low potential for bioaccumulation. Because most higher animals are able to metabolize methoxychlor, biomagnification is not expected to be significant (NRCC 1975; NAS 1977). The metabolites produced under such conditions, however, are not well characterized; hence, no assessment of the environmental significance is possible (Strachan 1985).

6.3.12.4.11.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654RP/84.

Bradshaw, J.S., E.L. Loveridge, K.P. Rippee, J.L. Peterson, D.A. White, J.R. Barton and D.K. Fuhriman. 1972. Pesticides in water. Seasonal variations in residues of chlorinated hydrocarbon pesticides in the water of the Utah Lake drainage system – 1970 and 1971. Pestic. Monit. J. 6: 166-170. (Cited in NRCC 1975.)

Charnetski, W.A., K.R. Depner and S. Beltaos. 1980. Distribution and persistence of methoxychlor in Athabaska River water. *In* Control of Black Flies in the Athabaska River. W.O. Haufe and G.C.R. Croome (eds.). Alberta Environment, Edmonton, Alberta. pp. 39-61. (Cited in NRCC 1983.)

Environment Canada. 1973. Pesticides Survey in Lakes Erie and Ontario, October 1973. For the Interdepartmental Working Group on Pesticide Research in the Great Lakes. Environmental Quality Coordination Unit, Canada Centre for Inland Waters, Burlington, Ontario. 27 pp. (Cited in NRCC 1975.)

Fredeen, F.J.H., J.G. Saha and M.H. Balba. 1975. Residues of methoxychlor and other chlorinated hydrocarbons in water, sand and selected fauna following injections of methoxychlor black fly larvicide into the Saskatchewan River in 1972. Pestic. Monit. J. 8: 241-246. (Cited in NRCC 1983.)

Kapoor, I.P., R.L. Metcalf, R.F. Nystrom and G.K. Sangha. 1970. Comparative metabolism of methoxychlor, methiochlor, and DDT in mouse, insects, and in a model ecosystem. J. Agric. Food Chem. 18: 1145-1152. (Cited in NAS 1977.)

Karickhoff, S.W. 1980. Sorption kinetics of hydrophobic pollutants in natural sediments. *In* Contaminants and Sediments. Vol. 2. R.A. Baker (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 193-206. (Cited in NRCC 1983.)

Kenaga, E.E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. Environ. Sci. Technol. 14: 553-556. (Cited in NRCC 1983.)

Lamoureux, C.H. and V.J. Feil. 1980. Gas chromatographic and mass spectrometric characterization of impurities in technical methoxychlor. J. Assoc. Off. Anal. Chem. 63: 1007-1037. (Cited in NRCC 1983.)

Lockhart, W.L., D.A. Metner and J. Solomon. 1977. Methoxychlor residue studies in caged and wild fish from the Athabaska River, Alberta, following a single application of black fly larvicide. J. Fish. Res. Board Can. 34: 626-632.

Mendel, J.L., A.K. Klein, J.T. Chen and M.S. Walton. 1967. Metabolism of DDT and some other chlorinated organic compounds by *Aerobacter aerogenes*. J. Assoc. Off. Anal. Chem. 50: 897-903. (Cited in NRCC 1983.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C.

NRCC. 1975. Methoxychlor: Its Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14102. 164 pp.

NRCC. 1983. Impact Assessments in Lotic Environments – Methoxychlor. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 20645. 130 pp.

Reinbold, K.A., I.P. Kapoor, W.F. Childers, W.N. Bruce and R.L. Metcalf. 1971. Comparative uptake and biodegradability of DDT and methoxychlor by aquatic organisms. Ill. Nat. Hist. Surv. Bull. 30: 405-417. (Cited in NAS 1977.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Strachan, W.M.J. 1985. Personal communication. Environmental Contaminants Division, National Water Research Institute, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario.

Wolfe, N.L., R.G. Zepp, D.F. Paris, G.L. Baughman and R.C. Hollis. 1977. Methoxychlor and DDT degradation in water: Rates and products. Environ. Sci. Technol. 11: 1077-1081.

Zepp, R.G., N.L. Wolfe, J.A. Gordon and R.C. Fincher. 1976. Light induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24: 727-733. (Cited in NRCC 1983.)

6.3.12.4.12 Mirex

6.3.12.4.12.1 Uses and Production

Mirex is used as an insecticide in the control of various ant species, particularly fire ants. Other uses, under the name Dechlorane, are as a flame retardant in plastics, as a smoke generator in pyrotechnics, in antifouling paints, rodenticides and antioxidants and in ablative, anthelmintic and lubricant compositions (Verschueren 1983).

Of the total amount of mirex sold up to 1975 by Hooker Chemicals and Plastics Corporation of Niagara Falls, New York, the principal manufacturer of mirex, 26% was for insecticidal use and the remainder for nonagricultural uses (IJC 1978).

An estimated 146 t of mirex were imported into Canada between 1963 and 1976. Mirex has not been used as an insecticide in Canadian agriculture (Health and Welfare Canada 1980). In 1981 and 1982, 8 and 14 t, respectively, of perchloropentacyclodecane were imported into Canada (Statistics Canada 1983).

In Canada, in December, 1978, the federal government prohibited the importation, manufacturing and processing of mirex for any uses that would lead to its dispersion into the environment (Environment Canada 1985).

Additional names for mirex that are used in Canada include Dechlorane and Perchloropentacyclodecane (Environment Canada 1985).

6.3.12.4.12.2 Sources and Pathways for Entering the Aquatic Environment

The main source from which mirex is released into the environment is the manufacturing process. Losses from the manufacture of mirex by Hooker Chemicals and Plastics Corporation and Armstrong Cork Corporation of Volney, New York, account for the mirex found in sediments of Lake Ontario. Kepone ($C_{10}Cl_{10}O$), a degradation product of mirex in the environment, has also been found in Lake Ontario biota; however, the source of contamination seems to be discharge from the manufacture of kepone rather than degradation of mirex (Verschueren 1983). Environmental losses did not occur at two Ontario manufacturing firms that import Dechlorane for use as a fire retardant in their products (Crabtree 1985). In 1979 and 1980 surveys of contaminants in treated water at treatment plant intakes in three cities along the Niagara River, mirex was not detected (detection limit 1 $ng \cdot L^{-1}$) in any of the 26 samples taken (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.12.4.12.3 Environmental Concentrations

In studying several raw and treated water samples from various sites, the Ontario Ministry of the Environment has not detected mirex (detection limit 5 $ng \cdot L^{-1}$) (Health and Welfare Canada 1980). Mirex residues in fresh and marine water samples in the United States have usually been at or below 10 $ng \cdot L^{-1}$ (Health and Welfare Canada 1980).

The source of mirex to the Lake Ontario ecosystem is two U.S. manufacturing and processing plants that discharge their wastes to the Niagara and Oswego Rivers, New York. The

Table 6-137. Environmental Concentration Ranges for Mirex in Canadian Surface Waters

Region	Concentration range[1] (ng·L^{-1})	Number of samples	Sampling year(s)
Western	ND[2]	1352	1980-1985
Central	ND-4	331	1980-1985
Atlantic	ND	48	1980-1985

[1] Detection limit is 1 ng·L^{-1}.

[2] ND = not detected.

Source: NAQUADAT 1985.

presence of mirex in sediments of Lake Ontario has been well documented (Verschueren 1983). The estimated amount of mirex in sediments of Lake Ontario is 688 kg, of which 366 kg were located in the Niagara River area and 224 kg in the Oswego River area (Verschueren 1983). Environmental concentration ranges for mirex in Canadian surface waters are presented in Table 6-137. Mirex was not detected (detection limit 1 ng·L^{-1}) in 58 samples taken in surface waters at four cities along the Niagara River in 1979 and 1980 surveys (Environment Canada/Ontario Ministry of the Environment 1981).

Environmental contamination by mirex has been manifested by its presence in aquatic and terrestrial birds and their eggs. Contamination of aquatic birds in the Maritimes and terrestrial birds in the Prairies and in the eastern provinces is probably associated with migration from the southeastern U.S.A. where mirex is used as a pesticide. In 1975, concentrations up to 5.54 mg·kg^{-1} lipid were found in wings of woodcocks from eastern Canada, and the highest mean value reported for birds from Ontario was 2.76 mg·kg^{-1}. The contamination of herring gull eggs is probably associated with mirex residues in adult gulls inhabiting the Lake Ontario region (Fisheries and Environment Canada/Health and Welfare Canada 1977).

Mirex has also been detected in fish. Fish species from Lake Ontario analyzed during 1975-1976 contained mirex residues, most of which were at concentrations below 0.1 mg·kg^{-1} (Fisheries and Environment Canada/Health and Welfare Canada 1977).

6.3.12.4.12.4 Forms and Fate in the Aquatic Environment

Mirex, 1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-1,3,4-methano-1H-cyclo-buta[c,d]pentalene, is a fully chlorinated caged-structure organic chemical with the empirical formula $C_{10}Cl_{12}$ and a molecular weight of 546 (Figure 6-26) (Alley 1972).

Mirex is relatively insoluble in water (7 μg·L^{-1} in pure water at 22°C) and has a low vapour pressure (0.8 mPa at 50°C) (Smith *et al.* 1978). It has been found to be extremely persistent in the environment (Kaiser 1978; Neely 1980), with sorption and bioaccumulation being the predominant environmental pathways. Numerous microcosm and field studies have demonstrated that biomagnification can be significant in the aquatic environment (Metcalf *et al.* 1973; Kaiser 1974; Kricher *et al.* 1975; Tagatz 1976; Cripe and Livingston 1977).

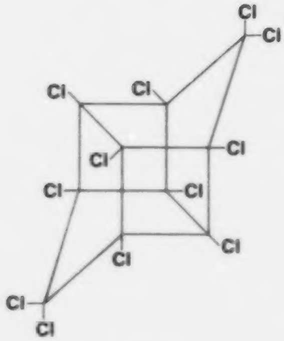


Figure 6-26. Mirex.

Mirex may be rapidly and quantitatively removed from the water column via sorption to organic material. Sorption partition coefficients of 10^5 have been measured under both laboratory and field conditions. Because the sorption partition coefficient of mirex is relatively high, the amount of mirex removed from the water column is expected to be high, with 93-98% of the mirex in an aquatic system associated with sediment material (Smith *et al.* 1978).

In the presence of light, mirex has been shown to undergo slow and structurally very limited reactions, with the production of photomirex ($C_{10}H_1Cl_{11}$), dihydro derivatives and kepone ($C_{10}Cl_{10}O$) (Alley *et al.* 1973, 1974a, b; Carlson *et al.* 1976). However, very little information is available on the rates of photolysis; hence, the environmental relevance of these reactions is unknown. The absorption of radiation by mirex above 290 nm is relatively weak. Mirex exposed to natural sunlight had a half-life of approximately 1 year (Smith *et al.* 1978).

Under certain conditions, volatilization may remove some mirex from the water column. A volatilization half-life of 21-333 d has been estimated, with the lower value representing low flow stream conditions. The rate of escape of mirex into the atmosphere as a result of volatilization, however, is expected to be very low, as the amount of mirex in solution will be small because of sorption to sediments (Smith *et al.* 1978).

Neither chemical oxidation nor hydrolysis is expected to be a significant process in the aquatic environment. Half-lives of several years have been estimated (Smith *et al.* 1978).

Mirex has been found to be generally resistant to biodegradation (Jones and Hodges 1974), although some studies have reported limited biodegradation under anaerobic conditions in sewage sludge (Andrade and Wheeler 1974; Andrade *et al.* 1975). Aerobic incubation of mirex with aerated effluents from sewage treatment plants and oil refineries for 6 weeks failed to demonstrate any significant biodegradation. In addition, incubation with an aqueous suspension of subsurface soils previously exposed to mirex and with an inoculum from an anaerobic sewage digestor did not degrade mirex (Smith *et al.* 1978).

Mirex is extremely persistent in the environment (Metcalf *et al.* 1973), and has been found in many aquatic organisms, including fish from the Great Lakes (Kaiser 1974). Fish testing by the Ontario Ministry of the Environment has found that mirex residues in fish tissue are found almost exclusively in Lake Ontario, the lower Niagara River and the St. Lawrence River (Crabtree 1985). Residues have also been detected in herring gull (*Larus argentatus*) eggs (Norstrom *et al.* 1978) and the eggs of numerous falcons (Kaiser 1978). A bioconcentration factor of more than 10^4 has been found for *Chlorococcum* sp. (alga) exposed to 1 $\mu g \cdot L^{-1}$ mirex (Hollister *et al.* 1975). Most of the available information on bioaccumulation and biomagnification comes from field studies, where mirex has been found to be a persistent contaminant in numerous components of aquatic food webs (Collins *et al.* 1973; Wolfe and Norment 1973; Naqvi and De La Cruz 1973; Borthwick *et al.* 1973; Kobylinski and Livingston 1975).

6.3.12.4.12.5 References

Alley, E.G. 1972. The use of mirex in the control of the imported fire ant. J. Environ. Qual. 2: 52-61.

Alley, E.G., D.A. Dollar, B.R. Layton and J.P. Minyard, Jr. 1973. Photochemistry of mirex. J. Agric. Food Chem. 21: 138-139.

Alley, E.G., B.R. Layton and J.P. Minyard, Jr. 1974a. Identification of the photo products of the insecticides mirex and kepone. J. Agric. Food Chem. 23: 442-445.

Alley, E.G., B.R. Layton and J.P. Minyard, Jr. 1974b. Photoreduction of mirex in aliphatic amines. J. Agric. Food Chem. 22: 727-729.

Andrade, P.S.L., Jr. and W.B. Wheeler. 1974. Biodegradation of mirex by sewage sludge organisms. Bull. Environ. Contam. Toxicol. 11: 415-416.

Andrade, P.S.L., Jr., W.B. Wheeler and D.A. Carlson. 1975. Identification of a mirex metabolite. Bull. Environ. Contam. Toxicol. 11: 473-479.

Borthwick, P.W., T.W. Duke, A.J. Wilson, Jr., J.I. Lowe, J.M. Patrick, Jr. and J.C. Oberheu. 1973. Accumulation and movement of mirex in selected estuaries of South Carolina, 1969-1971. Pestic. Monit. J. 7: 6-26.

Carlson, D.A., K.D. Konyha, W.B. Wheeler, G.P. Marshall and R.G. Zaylskie. 1976. Mirex in the environment: its degradation to kepone and related compounds. Science 194: 939-941.

Collins, D.A., J.R. Davis and G.P. Markin. 1973. Residues of mirex in channel catfish and other aquatic organisms. Bull. Environ. Contam. Toxicol. 10: 73-77.

Crabtree, P. 1985. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Cripe, C.R. and R.J. Livingston. 1977. Dynamics of mirex and its principal photo products in a simulated marsh system. Arch. Environ. Contam. Toxicol. 5: 295-303.

Environment Canada. 1985. Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa. 130 pp.

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Fisheries and Environment Canada/Health and Welfare Canada. 1977. Mirex in Canada. A Report of the Task Force on Mirex, April 1, 1977. Tech. Rep. 77-1. Ottawa.

Health and Welfare Canada. 1980. Pesticides. *In* Guidelines for Canadian Drinking Water 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 457-470.

Hollister, T.A., G.E. Walsh and J. Forester. 1975. Mirex and marine unicellular algae: accumulation, population growth and oxygen evolution. Bull. Environ. Contam. Toxicol. 14: 753-759.

IJC. 1978. Dodecachloropentacyclodecane (Mirex). *In* Group 2 – New and Revised Specific Water Quality Objectives. Proposed for the 1972 Agreement Between the U.S. and Canada on Great Lakes Water Quality. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario. pp. 68-77.

Jones, A.S. and C.S. Hodges. 1974. Persistence of mirex and its effects on soil microorganisms. J. Agric. Food Chem. 22: 435-439.

Kaiser, K.L.E. 1974. Mirex: an unrecognized contaminant of fishes from Lake Ontario. Science 185: 523-525.

Kaiser, K.L.E. 1978. The rise and fall of mirex. Environ. Sci. Technol. 12: 520-528.

Kobylinski, G.J. and R.J. Livingston. 1975. Movement of mirex from sediment and uptake by the hogchoker, *Trinectes maculatus*. Bull. Environ. Contam. Toxicol. 14: 692-698.

Kricher, J.C., J.C. Urey and M.L. Hawes. 1975. The effects of mirex and methoxychlor on the growth and productivity of *Chlorella pyrenoidosa*. Bull. Environ. Contam. Toxicol. 14: 617-620.

Metcalf, R.L., J.P. Kapoor, P.-Y. Lu, C.K. Schuth and P. Sherman. 1973. Model ecosystem studies of the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4: 35-44.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Naqvi, S.M. and A.A. De La Cruz. 1973. Mirex incorporation in the environment: residues in non-target organisms – 1972. Pestic. Monit. J. 7: 104-111.

Neely, W.B. 1980. A method for selecting the most appropriate environmental experiments on a new chemical. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 287-296.

Norstrom, R.J., D.J. Hallett and R.A. Sonstegard. 1978. Coho salmon (*Oncorhynchus kisutch*) and herring gulls (*Larus argentatus*) as indicators of organochlorine contamination in Lake Ontario. J. Fish. Res. Board Can. 35: 1401-1409.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.-W. Chow, D.C. Bomberger and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part II. Laboratory Studies. Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/7-78-074. 405 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tagatz, M.E. 1976. Effect of mirex on predator-prey interaction in an experimental estuarine ecosystem. Trans. Am. Fish. Soc. 105: 546-549.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Wolfe, J.L. and B.R. Norment. 1973. Accumulation of mirex residues in selected organisms after aerial treatment, Mississippi – 1971/1972. Pestic. Monit. J. 7: 112-116.

6.3.12.4.13 Toxaphene

6.3.12.4.13.1 Uses and Production

Toxaphene (camphechlor) has been widely used as a preharvest insecticide for cotton crops, cereal grains, oil seeds, vegetables, fruit and nut crops. It is currently used only for ectoparasitic control in sheep, cattle and pigs. Toxaphene replaced DDT in many agricultural uses, but this has now been prohibited in both Canada and the U.S.A. Another reported use was in fish eradication programs in lakes, but this was experimental only and is currently not a permitted use (Health and Welfare Canada 1980; IJC 1985).

In the United States, the annual production of toxaphene exceeded 45 000 t prior to its ban in 1982 (U.S. EPA 1980; IJC 1985). In Canada, toxaphene is no longer a registered pesticide, except as noted above. In the U.S.A., similar restrictions apply; since 1982, its use on cotton crops in the southeastern states, a major former application, has been negligible (IJC 1985).

An additional name for toxaphene is Hercules 3956 (IJC 1985).

6.3.12.4.13.2 Sources and Pathways for Entering the Aquatic Environment

Toxaphene can enter the aquatic environment at packing and processing plants (Health and Welfare Canada 1980), through its direct use on crops and animals and through direct application to water to remove undesirable fish (IJC 1985).

Recent studies have shown that toxaphene can be transported atmospherically to areas where it has never been used, such as the Great Lakes and the North Atlantic (Bidleman and Olney 1975; Rice and Evans 1984; IJC 1985).

6.3.12.4.13.3 Environmental Concentrations

Toxaphene concentrations in Lake Superior and Lake Huron range from 0.1 to 1.0 ng·L^{-1} (IJC 1981). In the United States, concentrations of toxaphene in natural waters are usually less than 1 μg·L^{-1}, although concentrations as high as 65 μg·L^{-1} were detected in surface waters several months after toxaphene had been applied to nearby cotton crops (Health and Welfare Canada 1980).

Toxaphene concentrations of 7.3-108.3 ng·L^{-1} were recorded for water samples collected in 1980 and 1981 along the shore of Lake Huron (Swain and Mullin 1986). A total toxaphene flux to Lake Michigan of 3.36-6.72 t was estimated for 1981 (Rice and Evans 1984).

Concentrations of toxaphene, sampled in 1980 in Lake Huron, ranged from 1.2 to 2.1 ng·L^{-1} and averaged 1.6 ng·L^{-1}. Concentrations of "toxaphene-like" residues in Siskiwit Lake on Isle Royale in Lake Superior were measured at 2.2 ng·L^{-1}, and, in Lake Superior adjacent to Isle Royale, at 1 ng·L^{-1} (Swain and Mullin 1986).

Atmospheric concentrations, ranging from the limit of detection (10^{-4} μg·m^{-3}) to 2.5 μg·m^{-3}, have been reported in areas where toxaphene was used for agricultural purposes in the United States (Health and Welfare Canada 1980). Comparative monitoring studies suggest that toxaphene is a prevalent atmospheric contaminant in areas where it is used, particularly in the southern United States (Stanley *et al.* 1971; U.S. EPA 1980). Toxaphene has been detected in several air samples collected in five North American cities, at concentrations of 0.04-7 μg·m^{-3}. A survey of organic substances in rainfall over Lake Superior in 1983 did not find toxaphene (Strachan 1985). There are reports of toxaphene at concentrations in the nanogram per cubic metre range over the Atlantic Ocean (Bidleman and Olney 1975; U.S. EPA 1980).

Soil concentrations of toxaphene in the United States range from 0.1 to 11.72 mg·kg^{-1}, with a mean value of 0.07 mg·kg^{-1} (Health and Welfare Canada 1980).

6.3.12.4.13.4 Forms and Fate in the Aquatic Environment

Toxaphene (camphechlor) is actually a complex mixture of largely uncharacterized chlorinated camphene and bornane derivatives. The mixture has a typical chlorine content of 67-69%, corresponding to an average empirical formula of $C_{10}H_{10}Cl_8$ and a molecular weight of 414. Gas chromatographic (GC) analysis has indicated the presence of at least 177 components in technical toxaphene, with approximately two-thirds of the mixture composed of compounds containing 7-9 chlorine atoms. Based on GC analysis, no one component appears to represent more than 5% of the total weight of the mixture (Holmstead *et al.* 1974). Because the mixture is composed of compounds having chlorinated bridged rings, toxaphene is frequently classified with a chlorinated cyclodiene, although the mixture has a different origin (i.e. photochemical chlorination of camphene) (Brooks 1974).

The water solubility of toxaphene is approximately 0.3 mg·L^{-1} at ambient temperatures, and the vapour pressure is 23-53 Pa at 25°C (Brooks 1974). Toxaphene has an estimated log octanol/water partition coefficient of 6.44 (Rice and Evans 1984).

Because toxaphene is a mixture of variously chlorinated compounds, all constituents do not have the same physical and chemical properties; hence, they do not have similar fates in the aquatic environment. As a consequence, the gas chromatographic analysis patterns of environmental samples differ substantially from analytical standards; therefore, quantitation is extremely difficult. Most information on aquatic fate is derived from studies that have examined total toxaphene. From the information available, it appears that toxaphene constituents are relatively stable chemically and biologically in the aquatic environment, with sorption and bioaccumulation being the dominant removal mechanisms (U.S. EPA 1979).

Hydrolysis, photolysis and oxidation do not appear to be important removal processes for toxaphene in the aquatic environment (Wolfe *et al.* 1976; U.S. EPA 1979). Although toxaphene is reported to undergo dehydrochlorination when exposed to ultraviolet light and strong sunlight (Brooks 1974), no environmentally relevant information is available.

Toxaphene has a high vapour pressure compared with other organochlorine compounds, and has been detected in the atmosphere in the vicinity of applications (Stanley *et al.* 1971), as well as in air that has been transported over extended distances (Bidleman and Olney 1975). Vaporization has been shown to be the major removal route of residues from foliage, with essentially no short-term loss attributable to biological or chemical degradation (Seiber *et al.* 1979).

Sorption to organic material is rapid and extensive. Sorption coefficients in the order of 10^3 have been found for bacteria, fungi and algae. The less soluble toxaphene constituents are preferentially sorbed by the microorganisms (Paris *et al.* 1977). Sorption and sedimentation have been found to remove toxaphene to the sediments (Veith and Lee 1971).

Bioaccumulation of toxaphene has been examined in laboratory and microcosm studies and in whole-lake surveys. Bioconcentration factors of 10^3 were found for algae, snails, mosquito larvae and fish in microcosm experiments (Sanborn *et al.* 1977). A geometric mean bioconcentration factor of 16 000 has been estimated from whole-body residue data for fish exposed to toxaphene in chronic laboratory experiments; equilibrium was reached in approximately 30 d of exposure. Bioconcentration factors ranged from 9000 to 19 000 for rainbow trout (*Salmo gairdneri*) and 4800 to 8000 for Atlantic salmon (*Salmo salar*), and averaged 15 000 for brook trout

(*Salvelinus fontinalis*). *Daphnia magna* accumulated 4000 times the water concentration of toxaphene (IJC 1985). Residues have been detected in several aquatic organisms. For example, concentrations of toxaphene in lake trout (*Salvelinus namaycush*) ranged from 1 to 10 mg·kg^{-1} (Rice and Evans 1984). Residues of "toxaphene-like" compounds in coho salmon (*Oncorhynchus kisutch*) skin-on fillets ranged in concentration from 0.5 mg·kg^{-1} in Lake Erie and Lake Superior to nearly 2 mg·kg^{-1} in Lake Michigan and Lake Huron (Clark *et al.* 1984). Concentration factors of 10^2 for aquatic plants, 10^3 for aquatic animals other than fish and 10^4 for fish were recorded for two lakes in Oregon (Terriere *et al.* 1966).

Toxaphene may be biologically transformed in anaerobic sediments (50% loss in 6 weeks). However, under aerobic conditions, no biotransformation appears to take place (Parr and Smith 1976). Persistence data from lake surveys indicate that transformation (chemical and biological) will occur fastest where the rate of transfer to anaerobic sediment is most rapid and where biologically rich systems are present. Shallow, biologically rich lakes have faster transformation rates than do deep oligotrophic lakes (Stringer and McMynn 1960; Johnson *et al.* 1966; Terriere *et al.* 1966; Veith and Lee 1971; Lee *et al.* 1977).

6.3.12.4.13.5 References

Bidleman, T.F. and C.E. Olney. 1975. Long range transport of toxaphene insecticide in the atmosphere of the western North Atlantic. Nature (London) 257: 475-477.

Brooks, G.T. 1974. Chlorinated Insecticides. Vol. 1. Technology and Applications. CRC Press, Cleveland, Ohio. 249 pp.

Clark, J.R., D. DeVault, R.J. Bowden and J.A. Weishaar. 1984. Contaminant analysis of fillets from Great Lakes coho salmon, 1980. J. Great Lakes Res. 10: 38-47.

Health and Welfare Canada. 1980. Toxaphene. *In* Guidelines for Canadian Drinking Water 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 633-643.

Holmstead, R.L., S. Khalifa and J.J. Casida. 1974. Toxaphene composition analyzed by combined gas chromatography – chemical ionization mass spectrometry. J. Agric. Food Chem. 22: 939-944. (Cited in U.S. EPA 1979.)

IJC. 1981. Committee on the Assessment of Human Health Effects of Great Lakes Water Quality. International Joint Commission, Windsor, Ontario. 142 pp.

IJC. 1985. Toxaphene. Draft Report, June. Aquatic Ecosystem Objectives Committee, Great Lakes Science Advisory Board, International Joint Commission, Windsor, Ontario.

Johnson, W.D., G.F. Lee and D.E. Spyridakis. 1966. Persistence of toxaphene in treated lakes. Air Water Pollut. 10: 555-560.

Lee, G.F., R.A. Hughes and G.D. Veith. 1977. Evidence for partial degradation of toxaphene in the aqueous environment. Water Air Soil Pollut. 8: 478-484.

Paris, D.F., D.L. Lewis and J.T. Barnett. 1977. Bioconcentration of toxaphene by microorganisms. Bull. Environ. Contam. Toxicol. 17: 564-572.

Parr, D.F. and S. Smith. 1976. Degradation of toxaphene in selected anaerobic soil environments. Soil Sci. 121: 52-57. (Cited in U.S. EPA 1979.)

Rice, C.P. and M.S. Evans. 1984. Toxaphene in the Great Lakes. *In* Toxic Contaminants in the Great Lakes. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, New York. pp. 163-194.

Sanborn, J.R., B.M. Francis and R.L. Metcalf. 1977. The degradation of selected pesticides in soil: A review of the published literature. U.S. NTIS PB-272-353. (Cited in U.S. EPA 1979.)

Seiber, J.N., S.C. Madden, M.M. McChesney and W.L. Winterlin. 1979. Toxaphene dissipation from treated cotton field environments: Component residual behaviour on leaves and in air, soil and sediments determined by capillary gas chromatography. J. Agric. Food Chem. 27: 284-291.

Stanley, C.W., J.E. Barney, III, M.R. Helton and A.R. Yobs. 1971. Measurement of atmospheric levels of pesticides. Environ. Sci. Technol. 5: 430-435.

Strachan, W.M.J. 1985. Organic substances in the rainfall of Lake Superior: 1983. Bull. Environ. Contam. Toxicol. 4: 677-683.

Stringer, G.E. and R.G. McMynn. 1960. Three years' use of toxaphene as a fish toxicant in British Columbia. Can. Fish Cult. 28: 37-44.

Swain, W.R. and M.D. Mullin. 1986. Long range transport of toxic organic contaminants to the Northern American Great Lakes. Manuscript in preparation.

Terriere, L.C., U. Kiigemagi, A.R. Gerlach and R.L. Borovicka. 1966. The persistence of toxaphene in lake water and its uptake by aquatic plants and animals. J. Agric. Food Chem. 14: 66-69. (Cited in U.S. EPA 1979.)

U.S. EPA. 1979. Toxaphene. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. 1. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 35-1 to 35-13.

U.S. EPA. 1980. Ambient Water Quality Criteria for Toxaphene. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-076.

Veith, G.D. and G.F. Lee. 1971. Water chemistry of toxaphene – role of lake sediments. Environ. Sci. Technol. 5: 230-234. (Cited in U.S. EPA 1979.)

Wolfe, N.L., R.G. Zepp, G.L. Baughman, R.C. Fincher and J.A. Gordon. 1976. Chemical and Photochemical Transformation of Selected Pesticides in Aquatic Systems. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA-600/3-76-067. 151 pp. (Cited in U.S. EPA 1979.)

6.3.12.5 Organophosphorus Compounds

6.3.12.5.1 Chlorpyrifos

6.3.12.5.1.1 Uses and Production

Chlorpyrifos (Dursban) is a wide-ranging nonsystemic insecticide that is effective as a contact, ingested and inhaled poison. It is used for the control of flies, household pests, mosquitoes (larvae and adults) and various crop pests in soil and on foliage. It is also used for the control of ectoparasites on cattle and sheep (Worthing 1983). Chlorpyrifos is registered in Canada for control of mosquitoes and agricultural pests, including bertha armyworms, cutworms, root maggots and chinch bugs (Marshall and Roberts 1978).

The consumption of chlorpyrifos in Canada between 1974 and 1976 amounted to $4\text{-}7 \times 10^4$ kg (as active ingredient); of this, 95% was used for the control of pests of tobacco crops, mainly in Ontario and Quebec, and for the control of mosquito larvae, mainly in the Prairie Provinces (Marshall and Roberts 1978). In 1981 and 1982, 186 and 513 t, respectively, of chlorpyrifos, as the formulated pesticide, were imported into Canada (Statistics Canada 1983).

Additional names for chlorpyrifos that are used in Canada include Dursban and Lorsban (Agriculture Canada 1984).

6.3.12.5.1.2 Sources and Pathways for Entering the Aquatic Environment

Chlorpyrifos enters the aquatic environment as a result of its direct application to water bodies and via leaching and surface runoff from treated terrestrial ecosystems. Applications of 0.2-2.2 kg·ai·ha^{-1} (ai = active ingredient) have been reported for treatment of tobacco crops. For the control of mosquito larvae, applications of 0.028-0.56 kg-ai·ha^{-1} have been used (Marshall and Roberts 1978).

6.3.12.5.1.3 Environmental Concentrations

With certain methods of application, chlorpyrifos in treated aquatic ecosystems may reach maximal concentrations during the initial phases of treatment, thereafter rapidly declining. There are indications that as much as 75-80% of the total quantity of chlorpyrifos (initial water concentration of 0.2 mg·L^{-1}) applied to small, shallow ponds can be lost in 5-15 d. The majority of chlorpyrifos remaining is rapidly adsorbed by sediments, whereupon an equilibrium is established with the overlying water. This results in a low concentration of chlorpyrifos that may be maintained in the water column for extended periods (Hurlbert *et al.* 1970; Marshall and Roberts 1978). When slow-release granular or pelleted formulations are used, initial high concentrations of chlorpyrifos are avoided. Using these formulations, relatively persistent residue levels can be found (up to 180 d) in both water and sediments (Marshall and Roberts 1978). Sampling results for chlorpyrifos are not reported in NAQUADAT (1985).

6.3.12.5.1.4 Forms and Fate in the Aquatic Environment

Chlorpyrifos (*0,0*-diethyl-*0*-(3,5,6-trichloro-2-pyridyl) phosphorothioate) is a colourless solid with a molecular weight of 350.5 and a melting point of 42-43.5°C (Figure 6-27). It has a water solubility of 2 mg·L^{-1} at 25°C, a vapour pressure of 2.5 mPa at 25°C and a calculated log octanol/water partition coefficient of 5.11 at 20°C (Worthing 1983; Verschueren 1983). Although few reliable quantitative data are available, chlorpyrifos may be sorbed, volatilized, hydrolyzed or biodegraded (Marshall and Roberts 1978).

As with other organophosphorus pesticides, chlorpyrifos may be readily hydrolyzed in water. Half-lives ranging from 10 to 100 d at temperatures between 15 and 35°C and at pH 5-9 have been reported (Marshall and Roberts 1978). Metal cations, such as ferrous, cadmium, lead and cupric ions, as well as some organic compounds have been found to accelerate the hydrolysis of chlorpyrifos (Marshall and Roberts 1978). In natural waters, the apparent degradation half-life may be much shorter (Schaefer and Dupras 1970). Principal hydrolytic products are 3,5,6-trichloro-2-pyridinol and phosphorothioic acid (Smith 1966; Brust 1966).

Sorption appears to be the primary nondegradative mechanism for chlorpyrifos removal in the aquatic environment (Marshall and Roberts 1978). Chlorpyrifos is quite lipophilic, and has a high degree of partitioning to organic matter (K_{ow} ~13 600). However, few quantitative data are available to assess the relative importance of sorption in the aquatic environment. Field surveys have indicated a tendency for chlorpyrifos to partition to sediment; hence, sediments are considered to be a major reservoir in aquatic systems (Marshall and Roberts 1978).

Although it has a low vapour pressure, chlorpyrifos is also sparingly soluble in water. Hence, in the absence of competition from sorption, some volatilization from shallow aqueous systems and from soil is anticipated (Blau and Neely 1975).

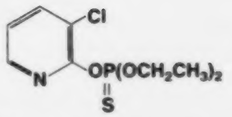


Figure 6-27. Chlorpyrifos.

Chlorpyrifos is degraded in soils. Half-lives of less than 1 and 2.5 weeks were found for degradation of chlorpyrifos (initial concentration 10 mg·L^{-1}) in nonsterilized sandy loam and organic soils, respectively. Alternatively, in sterilized sandy loam and organic soils, half-lives increased to 17 and more than 24 weeks, respectively (Miles *et al.* 1979).

Although no quantitative data are available on the metabolism of chlorpyrifos by invertebrates, field surveys and model ecosystem studies have indicated elevated tissue levels, suggesting a possible lack of metabolism. Fish, on the other hand, rapidly metabolize and excrete chlorpyrifos; calculated half-lives of 2.3-10 h have been reported for goldfish (*Carassius auratus*) and mosquitofish (*Gambusia affinis*) (Blau and Neely 1975; Marshall and Roberts 1978). Because chlorpyrifos has a high calculated octanol/water partition coefficient (log P_{ow} 5.11), some bioaccumulation is expected. Bioconcentration factors of 72 and 690 were found for algae and snails, respectively, in a model aquatic ecosystem (Metcalf 1974), and 11 for crayfish in an artificial stream (Brown 1975). Bioconcentration factors ranging from 310 to 640 for goldfish (Metcalf 1974; Branson *et al.* 1975) and mosquitofish (Smith *et al.* 1972) and up to 6000 for channel catfish (*Ictalurus punctatus*) have been reported.

6.3.12.5.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Blau, G.E. and W.B. Neely. 1975. Mathematical model building with an application to determine the distribution of Dursban insecticide added to a simulated ecosystem. Adv. Ecol. Res. 9: 133-162. (Cited in Marshall and Roberts 1978.)

Branson, D.R., W.B. Brock and G.A. Blau. 1975. Predicting a bioconcentration potential of organic chemicals from partitioning coefficients. *In* Symposium on Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. G.D. Veith and D.E. Konasewich (eds.). Great Lakes Advisory Board, International Joint Commission, March 11-13, Canada Centre for Inland Waters, Burlington, Ontario. pp. 99-118. (Cited in Marshall and Roberts 1978.)

Brown, J.R. 1975. The persistence and biological activity of diethyl-3,5,6-trichloro-2-pyridyl phosphorothioate (Dursban). Unpublished report. (Cited in Marshall and Roberts 1978.)

Brust, H.F. 1966. A summary of chemical and physical properties of Dursban. Down Earth 22: 21-22. (Cited in Marshall and Roberts 1978.)

Hurlbert, S.H., M.S. Mulla, J.O. Keith, W.E. Westlake and M.E. Dusch. 1970. Biological effects and persistence of Dursban in freshwater ponds. J. Econ. Entomol. 63: 43-52. (Cited in Marshall and Roberts 1978.)

Marshall, W.K. and J.R. Roberts. 1978. The Ecotoxicology of Chlorpyrifos. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16079. 314 pp.

Metcalf, R.L. 1974. A laboratory model ecosystem to evaluate compounds producing biological magnification. Essays Toxicol. 5: 17-28. (Cited in Marshall and Roberts 1978.)

Miles, J.R.W., C.M. Tu and C.R. Harris. 1979. Persistence of eight organophosphorus insecticides in sterile and non-sterile mineral and organic soils. Bull. Environ. Contam. Toxicol. 22: 312-318.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Schaefer, C.H. and E.M. Dupras, Jr. 1970. Factors affecting the stability of Dursban in polluted waters. J. Econ. Entomol. 63: 701-705. (Cited in Marshall and Roberts 1978.)

Smith, G.N. 1966. Basic studies on Dursban insecticide. Down Earth 22: 3-7. (Cited in Marshall and Roberts 1978.)

Smith, G.N., Y. Taylor and B.S. Watson. 1972. Ecological studies on chlorpyrifos. The Dow Chemical Company, Midland, Michigan. Unpublished report. (Cited in Marshall and Roberts 1978.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 125.

6.3.12.5.2 Diazinon

6.3.12.5.2.1 Uses and Production

Diazinon is a broad-spectrum contact insecticide and acaricide used primarily for crop protection, especially fruit trees, corn, tobacco and potatoes. Small amounts are used for the treatment of ornamental plants, domestic animals, lawns and gardens, and it is also used in households, food processing plants and warehouses (NAS 1977).

Data on the importation of diazinon into Canada are presented in Table 6-138.

Additional names for diazinon that are used in Canada include Basudin and Diazol (Agriculture Canada 1984).

6.3.12.5.2.2 Sources and Pathways for Entering the Aquatic Environment

Although no specific information exists, the predominant route of entry of diazinon into the aquatic environment is believed to be runoff from agricultural lands. Barring accidental spillage and spray drift, agricultural runoff should account for most occurrences of diazinon in aquatic systems (NAS 1977).

6.3.12.5.2.3 Environmental Concentrations

Limited information is available on diazinon in Canadian surface waters. Only two regions, Western and Atlantic, reported any sampling for diazinon in surface water in NAQUADAT (1985). The Atlantic region reported that 55 samples had diazinon concentrations below the detection limit (0.01 $\mu g{\cdot}L^{-1}$) during the sampling period prior to 1980. The Western region reported diazinon concentrations of less than 0.02 $\mu g{\cdot}L^{-1}$ (detection limit 0.01 $\mu g{\cdot}L^{-1}$) for 164 samples taken between 1980 and 1985 (NAQUADAT 1985).

6.3.12.5.2.4 Forms and Fate in the Aquatic Environment

Diazinon (*0,0*-diethyl-*0*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) (Figure 6-28) is a colourless liquid with a boiling point of 89°C at 10 Pa. It has a water solubility of 40 $mg{\cdot}L^{-1}$ at 20°C (Eto 1979; Verschueren 1983).

Table 6-138. Importation of Diazinon into Canada

Compound	Amount (t)	
	1981	1982
Diazinon, technical grade	124	115
Diazinon, formulated pesticide	7	–

Source: Statistics Canada 1983.

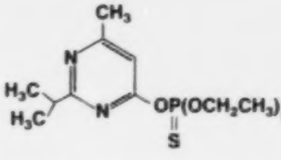


Figure 6-28. Diazinon.

Unlike other organophosphorus pesticides, diazinon is hydrolytically stable in neutral and alkaline aqueous systems. At pH 7.4 and 20°C, a half-life of 185 d has been reported; at pH 3.1, however, the hydrolytic half-life was reduced to 12 h (Menzie 1969; Eto 1979).

Diazinon is rapidly degraded in terrestrial environments; such decomposition is considered to be biologically mediated. For example, a 50% reduction of diazinon in sterile and nonsterile soil (pH 8.0) occurred in 12.5 weeks and less than 1 week, respectively. In sterile and nonsterile organic soil (pH 7.6), a 50% reduction of diazinon occurred after 6.5 and 2 weeks, respectively (Miles *et al.* 1979).

Diazinon may be bioaccumulated by some aquatic species under conditions of continuous exposure. The uptake and excretion of diazinon by several freshwater organisms have been studied under laboratory continuous-flow conditions (pH 6.8, alkalinity 32 $mg{\cdot}L^{-1}$ $CaCO_3$). Exposure to 10 $\mu g{\cdot}L^{-1}$ diazinon for 7 d resulted in steady-state bioconcentration factors ranging from approximately 5 to 17 for invertebrates [red snail (*Indoplanorbis exustus*), pond snail (*Cipangopoludina malleata*), crayfish (*Procambarus clarkii*)], whereas a range of 17-152 was found for freshwater fish [topmouth gudgeon (*Pseudorasbora* sp.), guppy (*Lebistes reticulatus*)]. Upon transfer to diazinon-free water, depuration was rapid, with levels rapidly declining in 7 d. A biological half-life for diazinon in gudgeon was estimated to be less than 1 d (Kanazawa 1978). Upon exposure to 20 $\mu g{\cdot}L^{-1}$ diazinon for 7 d in a continuous-flow system, equilibrium bioconcentration factors were found in several fish species: 26 for loach (*Misgurnus anguillicaudatus*), 63 for rainbow trout (*Salmo gairdneri*) and 120 for carp (*Cyprinus carpio*). Biological half-lives were less than 1 d (Seguchi and Asaka 1981).

6.3.12.5.2.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press, Inc., Boca Raton, Florida. 387 pp.

Kanazawa, J. 1978. Bioconcentration ratio of diazinon by freshwater fish and snails. Bull. Environ. Contam. Toxicol. 20: 613-617.

Menzie, C.M. 1969. Metabolism of Pesticides. Bureau of Sport Fisheries and Wildlife, U.S. Dep. of the Interior, Washington, D.C. Special Scientific Report No. 127. (Cited in NAS 1977.)

Miles, J.R.W., C.M. Tu and C.R. Harris. 1979. Persistence of eight organophosphorus pesticides in sterile and non-sterile mineral and organic soils. Bull. Environ. Contam. Toxicol. 22: 312-318.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

Seguchi, K. and S. Asaka. 1981. Intake and excretion of diazinon in freshwater fishes. Bull. Environ. Contam. Toxicol. 27: 244-249.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

6.3.12.5.3 Fenitrothion

6.3.12.5.3.1 Uses and Production

Fenitrothion is a broad-spectrum insecticide, effective against a wide variety of pests, such as penetrating, chewing and sucking insect pests. Its use in Canada is mainly for the control of spruce budworm. Aerial applications range from 138 to 413 g-ai (ai = active ingredient) in less than 4.2 L of liquid per hectare (NRCC 1975). Large amounts of fenitrothion may be injected into the atmosphere each year. For example, in New Brunswick in 1971, approximately 318 000 kg of fenitrothion were applied to 1.2×10^6 ha of pulpwood forest in a 4-week period (NRCC 1975). Data for the importation of fenitrothion into Canada are presented in Table 6-139.

Additional names for fenitrothion that are used in Canada include Accothion, Fumithion and Sumithion (Agriculture Canada 1984).

6.3.12.5.3.2 Sources and Pathways for Entering the Aquatic Environment

Fenitrothion enters the environment almost exclusively as a result of spray operations. It enters the aquatic environment as the result of spray drift, as well as from leaching and runoff from treated terrestrial ecosystems (Sundaram 1974; NRCC 1977). Direct contamination of surface water occurs when a water body is too small to be avoided by spray aircraft (NRCC 1975). Spray applications used in Canada are a single treatment of 280 g-ai·ha^{-1} or two treatments each of 210 g-ai·ha^{-1} (Armstrong 1985). Fenitrothion was detected in a tributary of the Nashwaak River, New Brunswick, 4 km from the nearest spray area, less than 2 h after spraying occurred (Eidt and Sundaram 1975).

6.3.12.5.3.3 Environmental Concentrations

There are few reports of fenitrothion in water or aquatic organisms, partly as a result of its rapid degradation in natural waters. Most reports of environmental residues come from monitoring operations conducted in conjunction with spray operations. In flowing waters, concentrations up to 75 µg·L^{-1} have been reported, but residues essentially disappear within 4 d (Penney 1971; Sundaram 1974; Lockhart *et al.* 1977). Stagnant waters can have concentrations as high as 700 µg·L^{-1}, but these also return to background within 4 d (Lockhart *et al.* 1973). The Atlantic region reported a concentration range of 0.01 (detection limit) to 20.6 µg·L^{-1} for fenitrothion, based on 211 samples taken prior to 1980 (NAQUADAT 1985). In a study conducted on three tributaries of the Nashwaak River, New Brunswick, it was found that at a spray application of 140-210 g·ha^{-1}, most peak concentrations for fenitrothion were lower than 15 µg·L^{-1} and diminished rapidly (Eidt and Sundaram 1975). No detectable (detection limit 3 ng·L^{-1}) fenitrothion concentrations were found in 12 pond sites in New Brunswick, sampled in 1983, which had been sprayed in the 1980, 1981 and/or 1982 spray seasons (Ayer *et al.* 1984).

Table 6-139. Importation of Fenitrothion into Canada

	Amount (t)		
Compound	1981	1982	1983
Fenitrothion, technical grade	472	492	NA[1]
Fenitrothion, formulated pesticide	331	515	545

[1] NA = not available.

Sources: Statistics Canada 1983, 1984.

6.3.12.5.3.4 Forms and Fate in the Aquatic Environment

Fenitrothion (*0,0*-dimethyl-*0*-methylthio-*m*-tolyl phosphorothioate) (Figure 6-29) is a liquid with a molecular weight of 261.19, a boiling point of 140-145°C at 13 Pa and a vapour pressure of 18 Pa at 20°C. Its solubility in water is 14 mg·L^{-1} at 20-25°C, and it has a calculated log octanol/water partition coefficient of 3.38 (Eto 1979; Verschueren 1983; Worthing 1983).

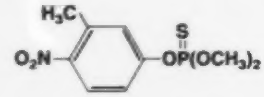


Figure 6-29. Fenitrothion.

Several studies have shown that fenitrothion degrades rapidly in natural waters (Sundaram 1973, 1974; NRCC 1975; Lockhart *et al.* 1977). For example, fenitrothion concentrations in water, suspended solids and sediment were found to be below detection limits (detection limit 50 ng·L^{-1}) 2 d after the spraying of a small pond in a spruce-fir forest in New Brunswick. The only identified products were *p*-nitro-*m*-cresol in water, which persisted less than 2 d, and aminofenitrothion in sediment, which persisted less than 4 d (Maguire and Hale 1980). Photolysis and microbial processes are believed to be the major mechanisms for the breakdown of fenitrothion in the aquatic environment (NRCC 1975; Miyamato 1977; Greenhalgh *et al.* 1980).

At approximately 20°C in neutral to slightly alkaline water (pH≤9), fenitrothion does not chemically hydrolyze to an appreciable extent (McKee and Wolf 1963). It was found to be stable in tap water at about pH 7 for 45 d (Zitko and Cunningham 1974). As the pH increases above 9, however, the rate of hydrolysis increases appreciably; the hydrolytic rate was found to increase 1000 times between pH 9.2 and 12.3 (Truchlick *et al.* 1972).

Fenitrothion is rapidly photolyzed in water. A photolytic half-life of 10 h was found for fenitrothion (6.18 $mg \cdot L^{-1}$) in distilled water under sunlight conditions. As the pH of aqueous solutions increased, photolysis also increased; half-lives of 50, 20 and 6 h at pH 3, 7 and 9, respectively, were reported. Photooxidation products included carboxy fenitrothion, fenitrooxon and formyl fenitrooxon (Miyamoto 1977). Fenitrothion sprayed on the surface of lake water held in open containers at 19-23°C and pH 7.0-7.5 for 14 d was removed with a half-life of 1.5-2 d (Greenhalgh *et al.* 1980). Fenitrothion is also rapidly photolyzed on soil surfaces; half-lives of 1.1 d have been recorded. When exposed to sunlight, fenitrothion in soil layers 2 mm in depth did not photodegrade rapidly; 50-150 d were required for 90% removal (Miyamoto 1977).

Volatilization of fenitrothion from true aqueous solutions is very slow (NRCC 1977; Maguire and Hale 1980). A half-life of 64 ± 5 d was found for volatilization from distilled water at 20°C. Volatilization decreased considerably ($t_{1/2}$>180 d) in the presence of 5 $mg \cdot L^{-1}$ fulvic acid. By contrast, the volatilization of fenitrothion from surface slicks on water appears to be quite rapid. Approximately 62% of the fenitrothion sprayed on the surface of distilled water was rapidly volatilized ($t_{1/2} = 18 \pm 6$ min) (Maguire and Hale 1980).

Fenitrothion may be rapidly microbially degraded in terrestrial and aquatic systems (Hirakoso 1969; Miyamoto 1972; Spillner *et al.* 1979). In a model aquatic ecosystem containing water and soil, fenitrothion was degraded, yielding a large variety of metabolites (Miyamoto *et al.* 1979). In terrestrial systems, half-lives ranged from 12 to 28 d, depending upon the soil type. Similar rates of biodegradation were found for submerged soils (Miyamoto 1977).

Little specific information is available on the bioaccumulation of fenitrothion by aquatic organisms. Bioconcentration factors of 181 for an alga, 69 for *Daphnia pulex*, 33 for snail (*Cipango paludina japonica* Martens) and 48 for carp (*Cyprinus carpio*) were found in a model aquatic ecosystem after exposure to fenitrothion for 21 d (Worthing 1983). Bioconcentration factors of 250, 230 and 200 were found for underyearling and yearling rainbow trout (*Salmo gairdneri*), and for topmouthed minnows (*Pseudorasbora parva*), respectively, upon exposure to fenitrothion (0.1 $\mu g \cdot L^{-1}$). Upon transfer to fenitrothion-free water, depuration was rapid with a 1000-fold decrease in residue levels within 5 d (Miyamoto 1977). A half-life of less than 1 d was reported for fenitrothion in trout (Lockhart *et al.* 1984).

6.3.12.5.3.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Armstrong, J.A. 1985. Personal communication. Pesticides Research Section, Research and Technical Services Directorate, Canadian Forestry Service, Agriculture Canada, Ottawa.

Ayer, W.C., G.L. Brun, D.C. Eid, W. Ernst, V.N. Mallet, R.A. Matheson and P.J. Silk. 1984. Persistence of Aerially Applied Fenitrothion in Water, Soil, Sediment and Balsam Fir Foliage. Maritime Forest Research Centre, Canadian Forestry Service, Fredericton, New Brunswick. Information Report M-X-153.

Eidt, D.C. and K.M.S. Sundaram. 1975. The insecticide fenitrothion in headwater streams from large-scale forest spraying. Can. Entomol. 107: 735-742.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press, Inc., Boca Raton, Florida. 387 pp.

Greenhalgh, R., K.L. Dhawan and P. Weinberger. 1980. Hydrolysis of fenitrothion in model and natural aquatic systems. J. Agric. Food Chem. 28: 102-105.

Hirakoso, S. 1969. Inactivating effects of microorganisms on insecticidal activity of Dursban. Jpn. J. Exp. Med. 39: 17-20. (Cited in NRCC 1975.)

Lockhart, W.L., D.A. Metner and N. Grift. 1973. Biochemical and residue studies on rainbow trout following field and laboratory exposures to fenitrothion. Monit. Entomol. 7: 26-36. (Cited in NRCC 1975.)

Lockhart, W.L., J.F. Flannagan, R.P. Moody, P. Weinberger and R. Greenhalgh. 1977. Fenitrothion monitoring in southern Manitoba. *In* Proc. Symp. on Fenitrothion: The Long-term Effects of its Use in Forest Ecosystems. J.R. Roberts, R. Greenhalgh and W.K. Marshall (eds.). National Research Council of Canada, Ottawa. NRCC No. 16073. pp. 233-252.

Lockhart, W.L., D.A. Menter, B.N. Billeck, G.P. Rawn and D.C.G. Muir. 1984. Bioaccumulation of some forestry pesticides in fish and aquatic plants. *In* Chemical and Biological Controls in Forestry. W.Y. Gardner and J. Harvey (eds.). Am. Chem. Soc. Symp. Ser. No. 238. pp. 298-315.

Maguire, R.J. and E.J. Hale. 1980. Fenitrothion sprayed on a pond: kinetics of its distribution and transformation in water and sediment. J. Agric. Food Chem. 28: 372-378.

McKee, J.E. and H.W. Wolf. 1963. Water Quality Criteria. 2nd edition. California State Water Resources Control Board, California Report 3-A. pp. 234-237.

Miyamoto, J. 1972. Metabolism of organophosphorus compounds and carbamate pesticides. Pestic. Chem. 6: 319-324.

Miyamoto, J. 1977. Degradation of fenitrothion in terrestrial and aquatic environments including photolytic and microbial reactions. *In* Proc. Symp. on Fenitrothion: The Long-term Effects of its use in Forest Ecosystems, J.R. Roberts, R. Greenhalgh and W.K. Marshall (eds.). National Research Council of Canada, Ottawa. NRCC No. 16073. pp. 105-134.

Miyamoto, J., Y. Takimoto and K. Mihara. 1979. Metabolism of organophosphorus insecticides in aquatic organisms, with special emphasis on fenitrothion. *In* Pesticide and Xenobiotic Metabolism in Aquatic Organisms. M.A.Q. Khan, J.J. Lech and J.J. Menn (eds.). Am. Chem. Soc. Ser. No. 99. pp. 3-20.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NRCC. 1975. Fenitrothion. The Effects of its Use on Environmental Quality and its Chemistry. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14104. 162 pp.

NRCC. 1977. Fenitrothion: The Long-term Effects of Its Use in Forest Ecosystems – Current Status. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 15389. 18 pp.

Penney, G.H. 1971. Summary Report on the Effects of Forest Spraying in New Brunswick in 1971 on Juvenile Atlantic Salmon and Aquatic Insects. Report supplied to the Panel by E.W. Burridge, Can. Fish. Serv., Environment Canada, Halifax, Nova Scotia. (Cited in NRCC 1975.)

Spillner, C.J., V.M. Thomas and J.R. Debaun. 1979. Effect of fenitrothion on microorganisms which degrade leaf-litter and cellulose in forest soils. Bull. Environ. Contam. Toxicol. 23: 601-606.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Sundaram, K.M.S. 1973. Degradation Dynamics of Fenitrothion in Aqueous Systems. Chemical Control Research Institute, Agriculture Canada, Ottawa. Information Report CC-X-44. 19 pp. (Cited in NRCC 1975.)

Sundaram, K.M.S. 1974. Distribution and Persistence of Fenitrothion Residues in Foliage, Soil and Water in Larose Forest. Chemical Control Research Institute, Agriculture Canada, Ottawa. Information Report CC-X-64. 43 pp. (Cited in NRCC 1975.)

Truchlick, S., I. Drabek, I. Kovac and S. Gager. 1972. Metathion – a new low-toxicity organophosphorus insecticide. *In* Proc. 3rd Conf. on Chemistry and Application of Organophosphorus Compounds. U.S. Dep. of Commerce. U.S. NTIS JPRS 57825. p. 129. (Cited in NRCC 1975.)

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 261.

Zitko, V. and T.D. Cunningham. 1974. Fenitrothion Derivatives and Isomers, Hydrolysis, Adsorption and Biodegradation. Fish. Mar. Serv. Tech. Rep. No. 458. 27 pp. (Cited in NRCC 1975.)

6.3.12.5.4 Glyphosate

6.3.12.5.4.1 Uses and Production

Glyphosate, introduced in 1971, is a nonselective, postemergence herbicide; its mono(isopropylammonium) salt (Roundup) is effective on deep-rooted perennial species and annual and biennial species of grasses, sedges and broad-leaved weeds (Eto 1979; Büchel 1983; Worthing 1983). Only one product is registered in Canada for commercial and domestic use for nonselective weed control on noncroplands (rights-of-ways, industrial sites, dry ditches, grass renovation, recreational lands, airports, etc.), and agricultural use for specified croplands (grain crops, potatoes, corn, soybeans, sugar beets, etc.) (Environment Canada/Ministère de l'Environnement du Québec 1984).

No importation data are available (Statistics Canada 1983), probably because there is only one registered agent for glyphosate in Canada and the data are withheld to protect its interests. Glyphosate was sold to Quebec farmers in 1982, but the amount was not quantified (Agriculture Canada 1985). Glyphosate was used in Ontario in 1983 (76 350 kg) for field crops, fruit and vegetable production and roadside use (Ontario Ministry of Agriculture and Food 1984).

Additional names for glyphosate that are used in Canada include *N*-(Phosphonomethyl)glycine, present as isopropylamine salt, and Roundup (Agriculture Canada 1984; Environment Canada/Ministère de l'Environnement de Québec 1984).

6.3.12.5.4.2 Sources and Pathways for Entering the Aquatic Environment

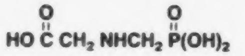
Glyphosate may enter the aquatic environment when applied as an aquatic herbicide, through spillage or accidental discharge or through possible waste disposal during production, packaging, storage and use. During its proper use in agriculture, forestry and horticulture, chances of aquatic contamination through terrestrial leaching or runoff appear remote, primarily because of glyphosate's rapid uptake by vegetation and its sorption to soil particles (Brønstad and Friestad 1985).

6.3.12.5.4.3 Environmental Concentrations

Little information is available on residues of glyphosate in the aquatic environment. The aerial application of 0.75 kg·ha⁻¹ glyphosate to a lake resulted in a surface water concentration of 0.7 mg·L⁻¹ immediately after treatment. No traces were detected in surface water 1 h after application (Lund-Høie 1985). Glyphosate has been used to control emergent and bankside weeds and floating weeds; application rates of about 1-10 kg·ha⁻¹ and 1-3.5 kg·ha⁻¹, respectively, have been reported. No information, however, is available on residues in the water column following treatment (Lund-Høie 1985). Sampling results for glyphosate are not recorded in NAQUADAT (1985).

6.3.12.5.4.4 Forms and Fate in the Aquatic Environment

Glyphosate, *N*-(phosphonomethyl)glycine (molecular weight 169.1) (Figure 6-30), is a colourless solid with a melting point of 200°C and a water solubility of 12 g·L⁻¹ at 25°C (Eto 1979; Büchel 1983; Worthing 1983). It is insoluble in most common organic solvents, and has a low octanol/water partition coefficient (6 × 10^{-4} at a glyphosate concentration of 20 mg·L⁻¹) (Tooby 1985). The mono(isopropylammonium) salt of glyphosate (Roundup) is much more water-soluble than is the parent acid.



$$\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\,\mathrm{CH_2}\,\mathrm{NHCH_2}\,\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OH)_2}$$

Figure 6-30. Glyphosate.

When applied to vegetation, glyphosate is rapidly absorbed by the foliage and translocated throughout the plant (Worthing 1983). It is strongly adsorbed onto soil particles where it may be decomposed, mainly via bacterial action (Worthing 1983; Grossbard and Atkinson 1985).

Among the various processes regulating the fate of glyphosate in the aquatic environment, the most significant are sorption to particulate matter and microbial degradation (Grossbard and Atkinson 1985).

Glyphosate is rapidly and quantitatively adsorbed to soil, with adsorption occurring through the phosphoric acid moiety. The organic matter content and soil pH appear to have little effect on adsorption; the addition of inorganic phosphate, however, can reduce adsorption (Tortensson 1985). Once in the soil, glyphosate appears to be practically immobile under normal conditions. At high pH and high levels of inorganic phosphate, mobility may be slightly increased (Tortensson 1985). Field and laboratory studies on leaching and runoff have demonstrated that glyphosate does not undergo extensive translocation (Rueppel *et al.* 1977; Edwards *et al.* 1980).

Chemical hydrolysis, oxidation and volatilization do not appear to be significant processes for the removal of glyphosate from the aquatic environment (Comes *et al.* 1976; Rueppel *et* *al.* 1977; Tortensson 1985; Brønstad and Friestad 1985; Tooby 1985). Laboratory irradiations of glyphosate in sterile, deionized water and sterile, natural water have indicated that some photolysis occurs; the environmental relevance of these studies, however, has yet to be established (Rueppel *et al.* 1977; Brønstad and Friestad 1985).

Microbial degradation appears to be the primary mechanism of destructive removal of glyphosate from both terrestrial and aquatic environments. Degradation occurs under both aerobic and anaerobic conditions. Rates of glyphosate degradation in soil have been found to vary considerably, with half-lives ranging from a few days to several months or years. Rates of degradation have been correlated not with any single soil factor, but with general microbial activity. The principal degradation product is aminomethylphosphonic acid (AMPA), which is also biologically degradable. The rate of AMPA degradation is usually slower than that of glyphosate, probably because of a stronger adsorption to particulate matter (Tortensson 1985).

Glyphosate is considered to dissipate rapidly from the water column. In laboratory studies, under either aerobic or anaerobic conditions, glyphosate was rapidly removed from nonsterile water with a half-life of less than 28 d (Rueppel *et al.* 1977). The major metabolite was AMPA. The half-life in a nonflowing model pond of 2-m diameter and 0.5-m depth was found to be approximately 12 d. In experiments using natural waters high in particulate matter and a rich microflora, glyphosate removal from the water column was found to be most rapid at low pH. A half-life of 7 weeks was found for glyphosate in aerobic water at pH 4.2 (Tooby 1985). In field studies, glyphosate was found to be rapidly removed from static pond water with a half-life of 12 h; this rapid dissipation was attributed to adsorption to particulate matter as well as microbial degradation (Tooby 1985). Depending upon the suspended solids loading and the microbial activity of flowing water, glyphosate may be transported several kilometres downstream from the site of aquatic application (Comes *et al.* 1976).

Accumulation of glyphosate by aquatic organisms is not expected to be significant. Bluegill sunfish (*Lepomis macrochirus*) exposed to 0.6 $mg \cdot L^{-1}$ for 28 d had a bioconcentration factor of 1.6. Exposure of rainbow trout (*Salmo gairdneri*), largemouth bass (*Micropterus salmoides*) and channel catfish (*Ictalurus punctatus*) for 14 d to 10 $mg \cdot L^{-1}$ glyphosate resulted in bioconcentration factors of 0.03, 0.04 and 0.18, respectively. Equilibrium conditions were reached by 7 d for the rainbow trout and largemouth bass, but not for the channel catfish. Elimination was rapid, with biological half-lives of 4-6 d for rainbow trout and largemouth bass (Sacher 1978a, b).

6.3.12.5.4.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Brønstad, J.O. and H.O. Friestad. 1985. Behaviour of glyphosate in the aquatic environment. *In* The Herbicide Glyphosate. E. Grossbard and D. Atkinson (eds.). Butterworth and Co. Publ. Ltd., London. pp. 200-205.

Büchel, K.H. (ed.). 1983. Chemistry of Pesticides. John Wiley & Sons, New York. 518 pp.

Comes, R.D., V.F. Bruns and A.D. Kelley. 1976. Residues and persistence of glyphosate in irrigation water. Weed Sci. 24: 47-50.

Edwards, W.M., G.B. Triplett, Jr. and R.M. Kramer. 1980. A watershed study of glyphosate transport in runoff. J. Environ. Qual. 9: 661-665.

Environment Canada/Ministère de l'Environnement du Québec. 1984. Les Pesticides en Agriculture au Québec en 1982. Service de la protection de l'environnement/Service de l'assainissement agricole, Montréal, Québec. 134 pp.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press Inc., Boca Raton, Florida. 387 pp.

Grossbard, E. and D. Atkinson (eds.). 1985. The Herbicide Glyphosate. Butterworth and Co. Publ. Ltd., London. 490 pp.

Lund-Høie, K. 1985. Efficacy of glyphosate in forest plantations. *In* The Herbicide Glyphosate. E. Grossbard and D. Atkinson (eds.). Butterworth and Co. Publ. Ltd., London. pp. 328-338.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of Agriculture and Food. 1984. Survey of Pesticide Use in Canada, 1983. Economics Information Rep. No. 84-05. 39 pp.

Rueppel, M.L., B.B. Brightwell, J. Schaefer and J.T. Marvel. 1977. Metabolism and degradation of glyphosate in soil and water. J. Agric. Food Chem. 25: 517-528.

Sacher, R.M. 1978a. Safety of Roundup in the Aquatic Environment. *In* Proc. Eur. Weed Res. Soc. 5th Symp. on Aquatic Weeds. Amsterdam, Netherlands. pp. 315-322. (Cited in Tooby 1985.)

Sacher, R.M. 1978b. Roundup, Seminar, Madrid. March 1978. pp. 3-23. (Cited in Tooby 1985.)

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Tooby, T.E. 1985. Fate and biological consequences of glyphosate in the aquatic environment. *In* The Herbicide Glyphosate. E. Grossbard and D. Atkinson (eds.). Butterworth and Co. Publ. Ltd., London. pp. 206-217.

Tortensson, L. 1985. Behaviour of glyphosate in soils and its degradation. *In* The Herbicide Glyphosate. E. Grossbard and D. Atkinson (eds.). Butterworth and Co. Publ. Ltd., London. pp. 137-150.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 303.

6.3.12.5.5 Guthion

6.3.12.5.5.1 Uses and Production

Guthion (azinphosmethyl) is a broad-spectrum, nonsystemic, persistent insecticide and acaricide, chiefly effective against biting and sucking insects (Worthing 1983; Agriculture Canada 1984). It is used commercially in the agricultural industry for the protection of specified fruits, vegetables, field crops, nuts, shade trees and forests (Eto 1979; Worthing 1983). Of the six registered products in Canada, only one can be used commercially, whereas the remaining five have restricted use on specified beans, fruits and vegetables and ornamental flowers, shrubs and trees (Statistics Canada 1984).

Data for the importation of guthion into Canada are presented in Table 6-140.

Table 6-140. Importation of Guthion into Canada

Compound	Amount (t) 1981	1982	1983
Guthion, technical grade	50	–	89
Guthion, formulated pesticide	67	50	30

Sources: Statistics Canada 1983, 1984.

6.3.12.5.5.2 Sources and Pathways for Entering the Aquatic Environment

Although data indicating the use patterns of guthion are scarce, the National Academy of Sciences (NAS 1975) reported approximately 1.2 × 10^6 kg were applied to agricultural areas in the U.S.A. in 1971.

Although no specific information is available concerning the movement of guthion after application, its relatively high solubility in water would indicate that leaching and runoff from agricultural lands would deposit significant amounts of guthion in water bodies (NAS 1975).

6.3.12.5.5.3 Environmental Concentrations

Information on guthion concentrations in Canadian surface waters is limited. The Atlantic and Western regions were the only regions to report guthion concentrations in NAQUADAT (1985). All of the 23 samples analyzed for guthion in the Atlantic region between 1980 and 1985 were below the detection limit of 0.1 $\mu g \cdot L^{-1}$. The 164 samples analyzed for guthion in the Western region between 1980 and 1985 had concentrations below 0.5 $\mu g \cdot L^{-1}$ (detection limit 0.1 $\mu g \cdot L^{-1}$) (NAQUADAT 1985). A preliminary investigation into the presence of agricultural pesticides in Manitoba watersheds in 1983 and 1984 revealed the presence of guthion in trace concentrations (<0.5 $\mu g \cdot L^{-1}$) in the LaSalle River (Williamson 1984).

6.3.12.5.5.4 Forms and Fate in the Aquatic Environment

Guthion (azinphosmethyl; *S*-(3,4-dihydro-4-oxobenzo[d]-[1,2,3] triazin-3-ylmethyl)- *O,O*-dimethyl phosphorodithioate) (Figure 6-31) is a colourless solid with a molecular weight of 317.3 and a melting point of 73-74°C. It is soluble in water (33 $mg \cdot L^{-1}$ at 20°C) (Worthing 1983; Verschueren 1983) and has a low vapour pressure (<1 μPa at 20°C) (Worthing 1983).

The only process governing the aquatic fate of guthion that has been systematically studied is hydrolysis (NAS 1977; IJC 1978). In a laboratory study, at environmental temperatures and pH, the hydrolytic half-life of guthion was estimated at 21-28 d (Heuer *et al.* 1974). The hydrolysis of guthion has, however, been shown to be pH-dependent, occurring more rapidly with increasing pH. Its half-life in both laboratory and natural water systems was found to be 30-70 d at a pH of 5.1-8.4 (Weiss and Gakstatter 1965).

Pond water studies have determined half-lives of 30 h (Flint *et al.* 1970) to 48 h (Meyer 1965); in aqueous laboratory solutions, the half-life of guthion was approximately 240 h (Flint *et al.* 1970) The more rapid disappearance of guthion from pond water has been attributed to photolysis and microbial action (IJC 1978).

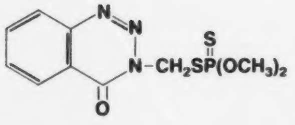


Figure 6-31. Guthion.

6.3.12.5.5.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press, Inc., Boca Raton, Florida. 387 pp.

Flint, D.R., O.D. Church, H.R. Shaw and J. Arman. 1970. Soil runoff, leaching and adsorption and water stability with guthion. Chemagro Report 28936. Kansas City, Missouri. (Cited in IJC 1978.)

Heuer, B., B. Yaron and Y. Birk. 1974. Guthion half-life in aqueous solutions and on glass surfaces. Bull. Environ. Contam. Toxicol. 11: 532-537.

IJC. 1978. Guthion. *In* Group 2 – New and Revised Specific Water Quality Objectives. Proposed for the 1972 Agreement Between the U.S. and Canada on Great Lakes Water Quality. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario. pp. 78-80.

Meyer, F.P. 1965. The experimental use of guthion as a selective fish eradicator. Trans. Am. Fish. Soc. 94: 203-209. (Cited in IJC 1978.)

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1975. Pest Control: An Assessment of Present and Alternative Technologies. Vol. 1. Contemporary Pest Control Practices and Prospects: The Report of the Executive Committee. National Academy of Sciences, U.S. National Research Council, Washington, D.C. (Cited in NAS 1977.)

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee. National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Weiss, C.M. and J.H. Gakstatter. 1965. The decay of anticholinesterase activity of organic phosphorus insecticides on storage in water of different pH. Proc. 2nd Int. Water Pollut. Res. Conf., August 1964, Tokyo. Adv. Water Pollut. Res. 1: 83-102. (Cited in NAS 1977.)

Williamson, D.A. 1984. A Preliminary Investigation into the Presence of Agricultural Pesticides in the La Salle and Assiniboine Rivers, Manitoba, Canada. Environmental Management Services Branch, Manitoba Department of Environment and Workplace Safety and Health. Water Standards and Studies Rep. No. 84-5.

Worthing, C.R. 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 26.

6.3.12.5.6 Malathion

6.3.12.5.6.1 Uses and Production

Malathion is a widely used, broad-spectrum, nonsystemic organophosphate insecticide and acaricide of low mammalian toxicity. It is used extensively in agriculture and horticulture. Malathion is also used to control animal ectoparasites, flies, household insects, human head and body lice and mosquitoes (Eto 1979; Mulla *et al.* 1981; Worthing 1983).

The most recent consumption data available are from 1977, when 345.3 t of malathion were sold as insecticides (not including fungicides) in Canada (Statistics Canada 1978). Figures for the importation of malathion into Canada are presented in Table 6-141.

An additional name for malathion that is used in Canada is Cythion (Agriculture Canada 1984).

6.3.12.5.6.2 Sources and Pathways for Entering the Aquatic Environment

Malathion may enter the aquatic environment through direct applications and surface runoff from treated areas. With its high water solubility, a significant portion of the malathion applied to terrestrial environments would be expected to enter the aquatic environment through leaching and runoff (NAS 1977). There are no data available to quantitate the transport of malathion from indirect sources, only from its direct application as a mosquito larvicide (Mulla *et al.* 1981).

6.3.12.5.6.3 Environmental Concentrations

Very little information is available relating to concentrations of malathion in the aquatic environment, possibly because of its rapid degradation. Concentrations of malathion as low as 13-19 ng·L^{-1} were found in stream water in cultivated areas in southern Ontario (Miles 1976). Only two regions, Atlantic and Western, reported malathion concentrations in NAQUADAT (1985). Of the 23 samples taken between 1980 and 1985 in the Atlantic region, all but 1 had concentrations below the detection limit (0.01 μg·L^{-1}). The only sample above the detection limit was taken from a lake in Nova Scotia in 1984 and had a concentration of 0.04 μg·L^{-1}. All 164 samples taken in the Western region between 1980 and 1985 had a malathion concentration below 0.05 μg·L^{-1} (NAQUADAT 1985).

6.3.12.5.6.4 Forms and Fate in the Aquatic Environment

Malathion (carbofos, *S*-1,2-bis(ethoxycarbonyl)ethyl-*O*,*O*-dimethyl phosphorodithioate) (Figure 6-32) is a yellow liquid with a molecular weight of 330.38, a melting point of 2.85°C and a boiling point of 156-157°C at 93 Pa. It is soluble in water (145 mg·L^{-1} at 25°C) and has a low vapour pressure (50 mPa at 20°C) (Eto 1979; Worthing 1983). A calculated log octanol/water partition coefficient of 2.89 has been reported (Verschueren 1983).

Malathion may readily undergo both hydrolysis and microbial degradation, and is considered to be relatively nonpersistent in terrestrial and aquatic environments (NAS 1977; Eto 1979; Mulla *et al.* 1981).

Malathion is hydrolyzed, as are other organophosphorus pesticides. The rate of hydrolytic degradation is at a minimum at pH 4. An increase in rate occurs with both higher and lower pH values. In water at 20°C, the hydrolytic half-life ranges from 40 d at pH 6 to 1 d at pH 8 (Wolfe *et al.* 1977).

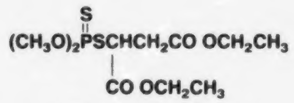
Exposure of malathion (10 μg·L^{-1}) in raw river water in a sealed glass jar to sunlight and artificial light resulted in 75% degradation in 1 week and 100% degradation in 4 weeks. It remained stable in distilled water for 3 weeks, indicating that degradation was biologically mediated (Eichelberger and Lichtenberg 1971). Malathion was rapidly degraded via carboxyesterase cleavage by salt-marsh bacteria (Bourquin 1975).

In a study with pinfish (*Lagodon rhamboides*), no bioaccumulation was observed after a 24-h exposure to 75 ng·L^{-1} malathion (Cook and Moore 1976). The uptake and metabolism of malathion were studied in the freshwater fish motsugo (*Pseudorasbora parva*) in aquarium water containing approximately 1 mg·L^{-1} malathion for 30 d. Malathion uptake was very low and metabolism was rapid; residue concentrations were less than 0.01 mg·L^{-1} 7 d after cessation of exposure (Kanazawa 1975). A half-life of 0.5 d was reported for malathion in carp (*Cyprinus carpio*) muscle (Bender 1969).

Table 6-141. Importation of Malathion into Canada

Compound	Amount (t) 1981	1982	1983
Malathion, technical grade	102	8	72
Malathion, formulated pesticide	111	58	248

Sources: Statistics Canada 1983, 1984.



$$(CH_3O)_2\overset{\overset{\displaystyle S}{\|}}{P}S\underset{\underset{\displaystyle CO\ OCH_2CH_3}{|}}{C}HCH_2CO\ OCH_2CH_3$$

Figure 6-32. Malathion.

6.3.12.5.6.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Bender, M.E. 1969. Uptake and retention of malathion by the carp. Prog. Fish Cult. 31: 155-159.

Bourquin, A.W. 1975. Microbial Malathion Interaction in Artificial Saltmarsh Ecosystems. Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-75-035.

Cook, G.H. and J.C. Moore. 1976. Determination of malathion, malaoxon, and mono- and dicarboxylic acids of malathion in fish, oyster and shrimp tissue. J. Agric. Food Chem. 24: 631-634. (Cited in Verschueren 1983.)

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press, Inc., Boca Raton, Florida. 387 pp.

Kanazawa, J. 1975. Uptake and excretion of organophosphorus and carbamate insecticides by freshwater fish, Motsugo, *Pseudorasbora parva*. Bull. Environ. Contam. Toxicol. 14: 346-352.

Miles, J.R.W. 1976. Insecticide residues on stream sediments in Ontario, Canada. Pestic. Monit. J. 10: 87-91. (Cited in Mulla *et al.* 1981.)

Mulla, M.S., L.S. Mian and J.A. Kawecki. 1981. Distribution, transport and fate of the insecticide malathion and parathion in the environment. Residue Rev. 81: 1-172.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1977. Drinking Water and Health. Safe Drinking Water Committee, National Academy of Sciences, U.S. National Research Council, Washington, D.C. 939 pp.
Statistics Canada. 1978. Sales of Pest Control Products by Canadian Registrants 1977. Catalogue No. 46-212.
Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.
Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.
Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.
Wolfe, N.L., R.G. Zepp, J.A. Gordon, G.L. Baugham and D.M. Cline. 1977. Kinetics of chemical degradation of malathion in water. Environ. Sci. Technol. 11: 88-93.
Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 337.

6.3.12.5.7 Parathion

6.3.12.5.7.1 Uses and Production

Parathion (actually diethyl parathion) and the more widely used methyl parathion are broad-spectrum, nonsystemic organophosphorus insecticides and acaricides with some fumigant action. They are used almost exclusively in the agricultural industry, on field, forage and vegetable crops. Parathion and methyl parathion have a wide spectrum of biological activity embracing both biting and sucking pests, and act as contact, stomach and respiratory poisons (Worthing 1983; Büchel 1983).

Parathion is registered for use as a pesticide in Canada; however, methyl parathion has not been registered in Canada for pesticide use since 1953 (Agriculture Canada 1984). Importation of parathion into Canada is presented in Table 6-142.

Additional names for parathion that are used in Canada include Folidol and Niran (Agriculture Canada 1984).

6.3.12.5.7.2 Sources and Pathways for Entering the Aquatic Environment

Because most parathion and methyl parathion is used in agriculture, and because of their relatively high water solubilities, it is probable that a significant amount will enter water bodies through spray drift, runoff and leaching. However, little specific information is available. Field studies have demonstrated that parathion can enter aquatic systems both through direct applications to control mosquitoes and other pests and indirectly from treated agricultural areas (Miles and Harris 1978; Mulla *et al.* 1981).

6.3.12.5.7.3 Environmental Concentrations

Concentrations of parathion and methyl parathion in water are generally quite low in the microgram per litre range and their persistence short-lived depending upon water pH, temperature and turbidity. Low pH and temperature and increased turbidity, in general, lead to greater persistence in the water column (Mulla *et al.* 1981). Methyl parathion and parathion have not been detected (detection limit 0.01 $\mu g \cdot L^{-1}$) in surface waters in the Atlantic and Western regions of Canada (NAQUADAT 1985).

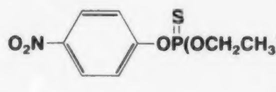
Table 6-142. Importation of Parathion into Canada

	Amount (t)		
Compound	1981	1982	1983
Parathion, technical grade	6	9	0
Parathion, formulated pesticide	8	15	15

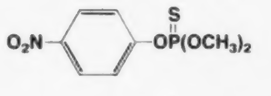
Sources: Statistics Canada 1983, 1984.

6.3.12.5.7.4 Forms and Fate in the Aquatic Environment

Parathion (diethyl parathion, *O,O*-diethyl-*O*-4-nitrophenylphosphorothioate) (Figure 6-33) is a pale yellow liquid with a molecular weight of 291.3 and a boiling point of 157-162°C at 80 Pa. It is soluble in water (24 $mg \cdot L^{-1}$ at 25°C) but has a low vapour pressure (5.0 mPa at 20°C) (Worthing 1983). Parathion is relatively stable in neutral or slightly acidic solutions, but rapidly hydrolyzes in alkaline solutions (Eto 1979; Verschueren 1983). Methyl parathion (dimethyl parathion, *O,O*-dimethyl-*O*-4-nitrophenylphosphorothioate) (Figure 6-33) is a white crystalline powder with a molecular weight of 263.2 and a melting point of 35-36°C. It is more soluble in water (55-60 $mg \cdot L^{-1}$) and appears to be less stable than parathion. Parathion and methyl parathion may be readily biodegraded, as are other organophosphorus pesticides. They are also subject to hydrolysis, photolysis and sorption in the aquatic environment (Smith *et al.* 1978).



Parathion



Methyl parathion

Figure 6-33. Parathion and methyl parathion.

Parathion and methyl parathion may be sorbed to both clays and soils in terrestrial and aquatic systems. Sorption partition coefficients of 5-30 have been reported, and roughly correlate with soil organic content (King and McCarty 1968; Saltzman and Yaron 1972). Methyl parathion sorption was demonstrated with several natural sediments and montmorillonite, with sorption partition coefficients of 46-60 and 100, respectively. Sorption to organic matter (heat-killed bacterial cells) was more extensive than sorption to inorganic matter, with sorption coefficients of 200-242 (Smith *et al.* 1978).

Because the phosphorus atom in organophosphorus compounds is electrophilic, both parathion and methyl parathion may be hydrolyzed. Hydrolytic half-lives of parathion and methyl parathion in an ethanol buffer solution (1:4) at pH 6 and

70°C were approximately 43 and 8 h, respectively (Eto 1979). Hydrolysis of methyl parathion (26 mg·L^{-1}) in natural water (<pH 8) proceeded with a half-life of approximately 17-19 d (Smith *et al.* 1978). Hydrolysis of methyl parathion yielded *0*-methyl-*0*-*p*-nitrophenylthiophosphoric acid and *p*-nitrophenol (Smith *et al.* 1978).

Both parathion and methyl parathion are biodegraded in terrestrial and aquatic environments (Graetz *et al.* 1970; Zuckermann *et al.* 1970; Eichelberger and Lichtenberg 1971; Munnecke and Hsieh 1974; Munnecke 1976). Parathion and methyl parathion (10 μg·L^{-1}) in raw river water in sealed glass jars (under sunlight and artificial fluorescent light) for 1 week degraded by 50 and 75%, respectively (Eichelberger and Lichtenberg 1971).

Log octanol/water partition coefficients of 3.81 and 2.04 for parathion and methyl parathion, respectively, have been calculated (Verschueren 1983). Because of their rapid degradation in the environment, however, significant bioaccumulation is not expected (Büchel 1983). The blue-green alga *Anacystis nidulans* and the green alga *Scenedesmus obliquus* concentrated parathion to 50 and 70 times the water concentration (1 mg·L^{-1}), respectively, when exposed for 7 d (Gregory *et al.* 1969). In a study of parathion persistence in a model cranberry bog, the freshwater mussel *Elliptio complanatus* was found to concentrate parathion (approximately 1 mg·kg^{-1}) within the first 24 h of application. Residue concentrations, however, dropped to 0.04 mg·L^{-1} after 144 h of treatment (Miller *et al.* 1966). Killifish (*Fundulus complanatus*) exposed to 0.02 mg·L^{-1} parathion concentrated the residue to 1.68 mg·kg^{-1}. Metabolism and elimination, however, were rapid (Miller *et al.* 1966). Similar observations were reported for mosquitofish (*Gambusia affinis*) (Mulla *et al.* 1966).

6.3.12.5.7.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Büchel, K.H. (ed.). 1983. Chemistry of Pesticides. John Wiley & Sons, New York. 518 pp.

Eichelberger, J.W. and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Eto, M. 1979. Organophosphorus Pesticides: Organic and Biological Chemistry. CRC Press, Inc., Boca Raton, Florida. 387 pp.

Graetz, D., G. Chesters, T.C. Daniel, L.W. Newland and G.B. Lee. 1970. Parathion degradation in lake sediments. J. Water Pollut. Control Fed. 42: R76-R94.

Gregory, W.W., Jr., J.K. Reed and L.E. Priester, Jr. 1969. Accumulation of parathion and DDT by some algae and protozoa. J. Protozool. 16: 69-71. (Cited in Mulla *et al.* 1981.)

King, P.H. and P.L. McCarty. 1968. A chromatographic model for predicting pesticide migration in soils. Soil Sci. 106: 248-261.

Miles, J.R.W. and C.R. Harris. 1978. Insecticide residue in water, sediments, and fish of the drainage system of the Holland Marsh, Ontario, Canada, 1972-75. J. Econ. Entomol. 71: 125-131. (Cited in Mulla *et al.* 1981.)

Miller, C.W., B.M. Zucherman and A.J. Charig. 1966. Water translocation of diazinon-C^{14} and parathion-S^{35} of a model cranberry bog and subsequent occurrence in fish and mussels. Trans. Am. Fish. Soc. 95: 345-349. (Cited in Mulla *et al.* 1981.)

Mulla, M.S., J.O. Keith and F.A. Gunther. 1966. Persistence and biological effects of parathion residues in waterfowl habitats. J. Econ. Entomol. 59: 1085-1090. (Cited in Mulla *et al.* 1981.)

Mulla, M.S., L.S. Mian and J.A. Kawecki. 1981. Distribution, transport and fate of the insecticides malathion and parathion in the environment. Residue Rev. 81: 1-172.

Munnecke, D.M. 1976. Enzymatic hydrolysis of organophosphate insecticides. A possible pesticide disposal method. Appl. Environ. Microbiol. 32: 7-13.

Munnecke, D.M. and D.P.H. Hsieh. 1974. Microbial decontamination of parathion and *p*-nitrophenol in aqueous media. Appl. Microbiol. 28: 212-217.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Saltzman, S. and B. Yaron. 1972. Parathion adsorption from aqueous solutions as influenced by soil components. Pestic. Chem. 6: 87-100. (Cited in Smith *et al.* 1978.)

Smith, J.C., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.-W. Chou, D.C. Bomburger and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part II. Laboratory Systems. Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia. pp. 248-293.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Verschueren, K. 1983. Handbook of Environmental Data in Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. 695 pp.

Zuckermann, B.N., K. Deubert, M. Mackiewicz and H. Gunner. 1970. Studies on biodegradation of parathion. Plant Soil 33: 273-281.

6.3.12.6 Pyridinium Compounds

6.3.12.6.1 Diquat and Paraquat

6.3.12.6.1.1 Uses and Production

Diquat is a postemergence contact herbicide used for weed and grass control in domestic gardens, along driveways and patios and around trees and hedges. Commercially, it is used for preharvest potato haulm destruction and/or canola desiccation and control of corn spurrey in oats, broadleaf weeds and grasses on noncroplands and general vegetation around buildings and walkways. Its use is restricted in the control of weeds in still or slow-moving water in farm ditches, dugouts and ponds and in lakes and canals. Six companies are registered to market eight diquat-containing products in Canada; four products are for domestic use, three are for commercial use and one is for restricted use only (Agriculture Canada 1985).

Paraquat is a nonselective and postemergent contact herbicide registered for use in situations similar to those for diquat. Commercial uses include conifer control for pasture renovation and application as a residual herbicide for use on asparagus, grapes, fruits and vegetables and noncroplands. Paraquat has a restricted use in the control of weeds, cattails, bullrushes and emerged grasses in or near irrigation and drainage ditches, ponds, lakes, streams and rivers. In Canada four companies are registered to market nine products (four domestic, four commercial and one restricted) containing paraquat (Agriculture Canada 1985).

In 1982, 119 t of formulated diquat herbicide were imported into Canada; no imports were reported for 1981. In 1981 and 1982, 42 and 245 t, respectively, of formulated paraquat herbicide were imported into Canada (Statistics Canada 1983).

Additional names for diquat that are used in Canada include Aquacide; Reglone; and Reglone A Liquid Herbicide. Additional names used for paraquat that are used in Canada include Gramoxone; Weedol; Gramoxone Liquid Agr Herbicide; and Terraklene Liquid Suspension Residual Herbicide (Agriculture Canada 1984; Environment Canada/Ministère de l'Environnement du Québec 1984).

6.3.12.6.1.2 Sources and Pathways for Entering the Aquatic Environment

Diquat and paraquat may be added directly to water for the control of aquatic weeds; typical applications result in initial concentrations of approximately 1 mg·L^{-1}. Sorption by inorganic and organic material rapidly decreases concentrations of these herbicides in the water column (Crzenda *et al.* 1966; Calderbank 1972). In a study of pesticide runoff from field applications, it was determined that 1.5% or less of the amount applied appeared in runoff. Pesticides strongly bound to clay particles, such as the bipyridinium herbicides, appeared mainly in the sedimentary phase of the surface runoff (Smith *et al.* 1978). Diquat and paraquat are both rapidly sorbed by soil, and, hence, it is expected that these herbicides are relatively immobile in terrestrial-aquatic systems (Coats *et al.* 1966; Grover *et al.* 1980).

6.3.12.6.1.3 Environmental Concentrations

Except during those periods immediately following application, concentrations of diquat and paraquat are very low or nondetectable in the water column. Rapid intake by aquatic plants and sorption to sediments following plant death and decay prevent the widespread distribution of diquat and paraquat throughout the water column (Coats *et al.* 1966; Grover *et al.* 1980). No sampling results for either diquat or paraquat have been reported in NAQUADAT (1985).

6.3.12.6.1.4 Forms and Fate in the Aquatic Environment

Diquat (1,1′-ethylene-2,2′-bipyridinium ion) and paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) (Figure 6-34) are bipyridinium herbicides that rapidly desiccate green plants, particularly dicotyledonous plants (Summers 1980; Büchel 1983; Worthing 1983). Diquat is formulated as the dibromide, whereas paraquat is formulated as the dichloride; both herbicidal salts are water-soluble (700 g·L^{-1} at 20°C) (Worthing 1983).

The solid dibromide salt of diquat decomposes at 300°C and has a vapour pressure below 13 μPa. Likewise, the dichloride salt of paraquat decomposes at 300°C and has a negligible vapour pressure at room temperature (Worthing 1983). Both herbicides are rapidly absorbed by green plant tissues which are then killed upon exposure to light. Upon contact with soil, the herbicides are considered to be inactivated (Worthing 1983; WHO 1984). Paraquat has an experimentally derived soil organic carbon partition coefficient (K_{oc}) of approximately 15 000. Bioconcentration factors of less than 1 and 1600 have been calculated based on water solubility and K_{oc}, respectively (Kenaga 1980).

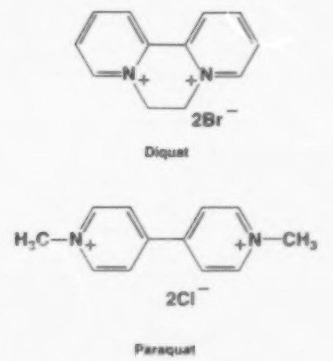


Figure 6-34. Diquat and paraquat.

Diquat and paraquat are usually rapidly dissipated from natural water systems via sorption by sediments and suspended material and by sorption and uptake by aquatic plants and algae (Summers 1980; Corwin and Farmer 1984). The herbicides may be released upon decay of plant tissue, becoming available for resorption by sediments (Summers 1980). Numerous studies in natural aquatic systems have shown that there is an initial rapid loss of diquat and paraquat from water. Initial concentrations of 1-5 mg·L^{-1} in natural waters usually decline to nondetectable levels between 8 and 27 d. Concentrations usually drop most rapidly within the first few days after application; the rate of dissipation appears to be slightly less rapid for paraquat than for diquat (Summers 1980). Both diquat and paraquat appear to be relatively persistent in the hydrosoils of aquatic systems and in the soils of terrestrial systems. Both herbicides are strongly adsorbed to clay particles. Once sorbed, desorption from soil particles appears to be slow (Weber *et al.* 1965; Coats *et al.* 1966). In soils and water containing organic matter, the herbicides may be sorbed by humic substances (Khan 1980; Narine and Guy 1982). Studies have shown that paraquat may migrate from soil organic matter to clay mineral particles and, hence, persist for significant periods of time in clay fractions. Strongly bound pesticides, such as the bipyridinium herbicides, may, under certain conditions, be transported laterally and vertically during soil erosion, runoff and leaching (Vinten *et al.* 1983). However, the extent and significance of such transport of strongly bound materials have not yet been elucidated. Diquat and paraquat that are strongly bound to sediments and bottom muds appear to be relatively unavailable for microbial decomposition (Summers 1980).

Aqueous solutions of diquat and, to a lesser extent, paraquat may be degraded in the presence of sunlight. Both herbicides have been found to be rapidly degraded on plant surfaces and in aqueous solutions in the presence of artificial ultraviolet light. Degradation is much slower in sunlight, however (Black *et al.* 1966; Slade and Smith 1967; Smith and Grove 1969; Calderbank and Slade 1976; Cavell 1979). In the presence of sunlight, aqueous solutions of paraquat underwent negligible degradation (Slade 1965), whereas 70% of the diquat was lost within 3 weeks (Smith and Grove 1969). Photochemical degradation on plant surfaces was greater, with 66% loss of paraquat within 3 weeks (Slade 1966) and 90% loss of diquat within 1 week (Calderbank 1968).

Diquat and paraquat have very low vapour pressures and are considered to be nonvolatile. Dry deposits of either herbicide exposed at room temperature showed no measurable loss after approximately 9 weeks (Coats *et al.* 1966). Chemical degradation is unlikely to be an important pathway for the removal of diquat and paraquat from the water column (Hance 1967).

Numerous soil microorganisms have been identified that are capable of degrading diquat and paraquat (Haley 1979); it has been concluded, however, that microbial degradation under field conditions would be slight, and would occur for only a short period of time following application (Burns and Audus 1970). Microbial degradation of strongly bound diquat and paraquat in soil has been found to be slow (Smith *et al.* 1976). Long-term field studies have, nonetheless, shown degradation rates of 5-10% per year, although this loss is probably not entirely the result of microbial degradation. Such a rate of loss from soil is considered to be greater than the rate required to prevent saturation of the deactivation capacity of soils (Hance *et al.* 1980; Moyer and Lindwall 1985). Depending upon soil conditions, the rate of loss of herbicides will vary. For example, 50% of the paraquat applied to an organic soil was lost 16 months after application (Khan *et al.* 1976). An orchard treated with paraquat (2.25 $kg \cdot ha^{-1}$, four times a year for 8 years) retained approximately 4-6 $mg \cdot kg^{-1}$ of the herbicide within the top 5 cm of soil (Khan *et al.* 1975). In another study, essentially all the paraquat applied to soil for 6 years was recovered in the top 5 cm of soil (Fryer *et al.* 1975).

Because paraquat and diquat are strongly bound to sediments and suspended particulate matter in the aquatic environment, few studies have been conducted on their fate in aquatic biota. Numerous studies have, however, been carried out on the toxicity of aqueous paraquat and diquat solutions to fish and other aquatic fauna (Summers 1980). From the available information, it does not appear that diquat or paraquat bioaccumulates to any significant degree in aquatic biota. Concentrations of diquat in adult bluegill sunfish (*Lepomis macrochirus*) residing in ponds subjected to a single treatment of diquat (1 $mg \cdot L^{-1}$ initial concentration) increased from 0.14 $mg \cdot kg^{-1}$ after 3 d to 0.49 $mg \cdot kg^{-1}$ after 10 d. Residue concentrations declined to 0.09 $mg \cdot kg^{-1}$ after 3 weeks and to nondetectable levels after 12 weeks (Gilderhus 1967). In a study using water free of suspended or bed sediments, diquat concentrations in rainbow trout (*Salmo gairdneri*) after a 24-h exposure to 0.5 and 1.5 $mg \cdot L^{-1}$ diquat were 0.25 and 1.63 $mg \cdot kg^{-1}$ (wet weight), respectively (Dodson and Mayfield 1979).

6.3.12.6.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Black, W.J.M., A. Calderbank, G. Douglas and R.H. McKenna. 1966. Residues in herbage and silage and feeding experiments following the use of diquat as a desiccant. J. Sci. Food Agric. 17: 506-509.

Büchel, K.H. (ed.). 1983. Chemistry of Pesticides. John Wiley & Sons, New York. 518 pp.

Burns, R.G. and L.J. Audus. 1970. Distribution and breakdown of paraquat in soil. Weed Res. 10: 49-58.

Calderbank, A. 1968. The bipyridylium herbicides. Effects on man. *In* Advances in Pest Control Research. Vol. 8. R.L. Metcalf (ed.). Interscience Publ., New York. pp. 127-135.

Calderbank, A. 1972. Environmental considerations in the development of diquat and paraquat as aquatic herbicides. Outlook Agric. 7: 51-54.

Calderbank, A. and P. Slade. 1976. Diquat and paraquat. *In* Herbicide Chemistry, Degradation and Mode of Action. P.C. Kearne and D.D. Kaufman (eds.). Marcel Dekker, New York. pp. 501-540.

Cavell, B.D. 1979. Methods used in the study of the photochemical degradation of pesticides. Pestic. Sci. 10: 177-180.

Coats, G.E., H.H. Funderburk, J.M. Lawrence and D.E. Davis. 1966. Factors affecting persistence and inactivation of diquat and paraquat. Weed Res. 6: 58-66.

Corwin, K.L. and W.J. Farmer. 1984. Nonsingle-valued adsorption-desorption of bromacil and diquat by freshwater sediments. Environ. Sci. Technol. 18: 507-514.

Crzenda, A.R., H.P. Nicholson and W.S. Cox. 1966. Persistence of four herbicides in pond water. J. Am. Water Works Assoc. 58: 326-332.

Dodson, J.J. and C.I. Mayfield. 1979. Modification of the rheotropic response of rainbow trout (*Salmo gairdneri*) by sublethal doses of the aquatic herbicides diquat and simazine. Environ. Pollut. 18: 147-157.

Environment Canada/Ministère de l'Environnement du Québec. 1984. Les Pesticides en Agriculture au Québec en 1982. Service de la protection de l'environnement/Service de l'assainissement agricole, Montréal, Québec. 134 pp.

Fryer, J.D., R.J. Hance and J.W. Ludwig. 1975. Long-term persistence of paraquat in a sandy loam soil. Weed Res. 15: 189-194.

Gilderhus, P.A. 1967. Effects of diquat on bluegills and their food organisms. Prog. Fish Cult. 29: 67-74.

Grover, R., A.E. Smith and H.C. Korven. 1980. A comparison of chemical and cultural control of weeds in irrigation ditchbanks. Can. J. Plant Sci. 60: 185-195.

Haley, T.J. 1979. Review of the toxicology of paraquat (1,1-dimethyl-4,4-dipyridylium chloride). Clin. Toxicol. 14: 1-46.

Hance, R.J. 1967. Decomposition of herbicides in the soil by non-biological chemical processes. J. Sci. Food Agric. 18: 544-547.

Hance, R.J., T.H. Byast and P.D. Smith. 1980. Apparent decomposition of paraquat in soil. Soil Biol. Biochem. 12: 447-448.

Kenaga, E.E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotoxicol. Environ. Lett. 4: 26-38.

Khan, S.U. 1980. Determining the role of humic substances in the fate of pesticides in the environment. J. Environ. Sci. Health 15: 1071-1090.

Khan, S.U., P.B. Marriage and W.J. Saidak. 1975. Residues of paraquat in an orchard soil. Can. J. Soil Sci. 55: 73-75.

Khan, S.U., A. Belanger, E.J. Hogue, H.A. Hamilton and S.P. Mathur. 1976. Residues of a paraquat and linuron in an organic soil and their uptake by onions, lettuce and carrots. Can. J. Soil Sci. 56: 407-412.

Moyer, J.R. and C.W. Lindwall. 1985. Persistence and availability of paraquat in a Lethbridge clay loam soil. Can. J. Soil Sci. 65: 523-529.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Narine, D.R. and R.D. Guy. 1982. Binding of diquat and paraquat to humic acid in aquatic environments. Soil Sci. 133: 356-363.

Slade, P. 1965. Photochemical degradation of paraquat. Nature (London) 207: 515.

Slade, P. 1966. The fate of paraquat applied to plants. Weed Res. 6: 158-167.

Slade, P. and A.E. Smith. 1967. Photochemical degradation of diquat. Nature (London) 213: 919-920.

Smith, A.E. and J. Grove. 1969. Photochemical degradation of diquat in dilute aqueous solution and on silica gel. J. Agric. Food Chem. 17: 609-613.

Smith, C.N., R.A. Leonard, G.W. Langdale and G.W. Bailey. 1978. Transport of Agricultural Chemicals from Small Upland Piedmont Watersheds. National Technical Information Service, Springfield, Virginia. NTIS Rep. No. PB-285/134. p. 386. (Cited in WHO 1984.)

Smith, S.N., A.J. Lyon and I.B. Sahid. 1976. The breakdown of paraquat and diquat by soil fungi. New Phytol. 77: 735-740.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Summers, L.A. 1980. The Bipyridinium Herbicides. Academic Press, London, U.K. 449 pp.

Vinten, A.J.A., B. Yaron and P.H. Nye. 1983. Vertical transport of pesticides into soil when adsorbed on suspended particles. J. Agric. Food Chem. 31: 662-664.

Weber, J.B., P.W. Perry and R.P. Upchurch. 1965. The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D and prometone by clays, charcoal, and an anion-exchange resin. Soil Sci. Soc. Am. Proc. 29: 678-688.

WHO. 1984. Paraquat and Diquat. Environmental Health Criteria 39. World Health Organization, Geneva. 181 pp.

Worthing, C.R. 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. pp. 223 and 418.

6.3.12.7 Triazine Compounds

6.3.12.7.1 Atrazine

6.3.12.7.1.1 Uses and Production

Atrazine is used for the pre- and postemergence control of annual broadleaf and grass weeds. In Canada, it is applied primarily on corn. Other uses include the treatment of turf grasses, and asparagus and forestry applications (U.S. EPA 1975; Worthing 1983; Verschueren 1983).

In Canada, there are currently 19 companies that market 4 domestic and 50 commercial products containing atrazine. Domestic uses include the control of algae in aquariums and ornamental ponds and application as a soil sterilant around driveways, patios, fencelines, etc. Commercial uses include the control of weeds, primarily grass weeds, in corn and application as a soil sterilant on noncroplands, such as airfields, parking lots and industrial sites (Agriculture Canada 1985).

A survey of the amount of pesticides sold to Quebec farmers in 1982 revealed that triazines and triazoles, which include atrazine, were the largest group of pesticides sold, for a total of 570.8 t. Individual pesticides, such as atrazine, were not quantified (Environment Canada/Ministère de l'Environnement du Québec 1984). In Ontario, a total of 1 729 680 kg of atrazine (as active ingredient) was used for agriculture and roadsides in 1983. This was the most heavily used pesticide in Ontario in that year (Ontario Ministry of Agriculture and Food 1984). In 1981 and 1982, 2088 and 1719 t, respectively, of formulated atrazine herbicide were imported into Canada. Also in 1981 and 1982, 469 and 736 t, respectively, of technical-grade atrazine were imported into Canada (Statistics Canada 1983).

Additional names for atrazine that are used in Canada include Aatrex (Agriculture Canada 1984); Aatrex Liquid; Aatrez Mine-0; Aetrex Plus; Aatrex 90W; Calmix 5; Chipman Atra-Mix Agrazine-Oil Concentrate Flowable Herbicide; Chipman Atrazine Flowable; Chipman Atrazine 80W Wettable Powder Herbicide; Chipman Atrazine 90W Wettable Powder Herbicide; Co-op Atrazine 5L Flowable Agr Herbicide; Co-op Atrazine 90W Herbicide; Ekko 80W Agr Herb; Laddok; Marzone Atrazine 80W Agr Herb; Niagara Liquid Atrazine; Niagara Atrazine 80W Agr Herbicide; Pfizer Atrazine 500; Pfizer Atrazine 80W Agr Herbicide; Primextra; Shell Atrazine 500L; Shell Atrazine 80W; Shell Atrazine 90W; Shell Blazine Liquid Herbicide; and Shell Blazine 80W Agr Herbicide (Environment Canada/Ministère de l'Environnement du Québec 1984).

6.3.12.7.1.2 Sources and Pathways for Entering the Aquatic Environment

Atrazine may enter the aquatic environment during production, spillage, use and disposal. Approximately 1% of the atrazine applied to agricultural land may ultimately enter nearby aquatic systems via runoff, drainage and spills (Muir *et al.* 1978; Triplett *et al.* 1978; Frank *et al.* 1979; Frank and Sirons 1979; Wu 1980). The majority of atrazine loss via surface runoff occurs immediately following application (usually at the end of June and July) and during rainstorm runoff events (Muir *et al.* 1978; Triplett *et al.* 1978; Frank and Sirons 1979; Wu 1980). Atrazine losses were found to vary from 0.1 to 2.9% of the amount applied in five rivers draining agricultural areas in Quebec (Muir *et al.* 1978). Soil type influences loss of atrazine in surface runoff; for example, losses ranging from a low of 0.33% from sandy soils to a high of 1.93% from clay soils were found in 11 agricultural watersheds in southern Ontario (Frank and Sirons 1979).

Atrazine has also been detected in groundwater. In Nebraska, water from 41 monitoring wells in an agricultural area contained atrazine at concentrations of 0.01-8.29 μg·L^{-1}. The soils were sandy and well drained, and had been treated with atrazine for 15 years at approximately 5.5 g·ha^{-1} (Wehtje *et al.* 1983). No atrazine was detected in groundwater in corn production areas in southern Ontario (Frank and Sirons 1979).

6.3.12.7.1.3 Environmental Concentrations

In agricultural areas where corn is treated with atrazine, usual applications range from 1 to 2 kg·ai·ha^{-1} (ai = active ingredient) (Frank and Sirons 1979). Atrazine was found in 80% of the streams draining agricultural watersheds (mean concentration 1.4 μg·L^{-1}) in southern Ontario (Frank and Sirons 1979). Atrazine, at a mean concentration of 1.6 μg·L^{-1}, was found in 77% of 92 samples of stream water collected from 12 streams on the Canadian side of the Great Lakes. No detectable residues (detection limit 0.05 μg·g^{-1}) were found in suspended solids, indicating that atrazine was transported in water of pH 6.5-8.5 in soluble form (Frank *et al.* 1979). Atrazine was found in three rivers in southern Ontario where it is used routinely. Concentrations of 0.05-30 μg·L^{-1}, 0.02-2.7 μg·L^{-1} and 0.02-1.0 μg·L^{-1} were found in the Thames, Grand and Saugeen rivers, respectively (Ralston 1986). Atrazine concentrations ranged from 0.01 to 26.9 μg·L^{-1} in five rivers draining agricultural areas in Quebec (Muir *et al.* 1978). Runoff from corn fields in Maryland contained atrazine in concentrations ranging from nondetec-

Table 6-143. Environmental Concentration Ranges for Atrazine in Canadian Surface Waters

Region	Concentration range ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Central	$ND^{1,2}$-0.13	71	Prior to 1980
	ND^{3}-0.02	59	Prior to 1980
	ND^{4}-0.02	71	Prior to 1980

[1] ND = not detected.
[2] Detection limit is 0.1 $\mu g \cdot L^{-1}$ (atrazine total).
[3] Detection limit is 0.02 $\mu g \cdot L^{-1}$ (deisopropylated atrazine).
[4] Detection limit is 0.02 $\mu g \cdot L^{-1}$ (de-ethylated atrazine).

Source: NAQUADAT 1985.

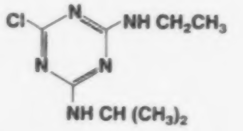


Figure 6-35. Atrazine.

table (detection limit 0.08 $\mu g \cdot L^{-1}$) to 52 $\mu g \cdot L^{-1}$ (Wu 1980). Concentrations of atrazine ranging from 0.01 to 8.29 $\mu g \cdot L^{-1}$ were found in groundwater in Nebraska (Wehtje *et al*. 1983).

Environmental concentration ranges for atrazine in Canadian surface waters are presented in Table 6-143. The Central region was the only region to report atrazine concentrations in NAQUADAT (1985).

6.3.12.7.1.4 Forms and Fate in the Aquatic Environment

Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine (Figure 6-35) is a colourless powder melting at 175-177°C. It has a volatility of 40 µPa at 20°C and a water solubility of 30 $mg \cdot L^{-1}$ at 20°C. It forms salts with acids and has a pK_a of 1.7 (Worthing 1983; Verschueren 1983).

Atrazine has an experimentally derived soil organic carbon adsorption coefficient (K_{oc}) of 149 and predicted bioconcentration factors of 86 (based on water solubility) and 7 (based on octanol/water partitioning) (Kenaga 1980). Its calculated log octanol/water partition coefficient is 3.32 (Lynch *et al*. 1985). There are some indications that *N*-nitrosamines may be formed from atrazine in soil and groundwater (Wolfe *et al*. 1976).

Atrazine is reversibly sorbed to soil particles (U.S. EPA 1975). When aqueous solutions of atrazine were exposed to wet sediments (mixtures of clay and silt, organic carbon content 5-40%, pH 4.4-7.7), initial sorption was rapid. Approximately 75% of the equilibrium concentration was sorbed within 3-6 min. Desorption with water was equally rapid, with sorption being completely reversible within 2 h. Experimentally derived soil adsorption coefficients (24-h K_d) ranged from 1.2 to 21; the organic carbon partition coefficients (K_{oc} based on K_d) ranged from 43 to 827 indicating a relatively low level of sorption affinity (Wauchope and Myers 1985). In a continuous-flow model ecosystem containing sediment, water and plankton, atrazine (at microgram per litre concentrations) showed no significant sorption even after 50 d of continuous exposure (Brockway *et al*. 1984). Field surveys have verified the lack of sorption of atrazine in flowing systems; suspended solids collected from 12 streams entering the Great Lakes contained no detectable residues of atrazine (detection limit 0.05 $\mu g \cdot g^{-1}$) (Frank *et al*. 1979). Conversely, atrazine may be found in the sediments of still waters. Application of atrazine to 0.5-ha farm ponds (≃pH 7-8, alkalinity 75-210 $mg \cdot L^{-1}$) resulted in deposition of atrazine to the pond sediments; no preferential concentration was found in the bottom sediments (Klassen and Kadoum 1979). It is concluded, therefore, that atrazine is not appreciably sorbed by sediments; any sorption that does take place appears to be temporary.

The maximum absorption of light by atrazine occurs at 220 nm. Although little reliable information is available, atrazine has been found to slowly photodegrade in pure form when deposited on surfaces and soil particles (Jordan *et al*. 1970). Irradiation with artificial light (>290 nm) of aqueous atrazine solutions (10 $mg \cdot L^{-1}$) at an initial pH of 6.8 and temperature of 15°C resulted in a photodegradation half-life of approximately 25 h. The presence of a photosensitizer such as acetone (~8 $mg \cdot L^{-1}$) decreased the half-life of atrazine to 4.9 ± 0.5 h. Major photoproducts were identified as de-*N*-alkylated derivatives (Burkland and Guth 1976). Field studies that have attempted to elucidate the environmental significance of photodecomposition of atrazine have not adequately considered other possible competing degradation or removal mechanisms.

Atrazine is not expected to volatilize to a significant extent under environmental conditions. Pure atrazine, spread on metal plates and held at room temperature, was slowly removed (2% in 5 h, 8% in 7 d, 31% in 36 d) (Davis *et al*. 1963). Approximately 25% of the atrazine applied to soils was lost in 24-48 h at 35°C; removal increased with sand content, but decreased with organic matter and clay content (Kearney *et al*. 1964). Whereas atrazine was found to readily volatilize from foliar surfaces (50% loss after 2 d at 40°C), it was not as readily removed from soil (10% loss after 2 d at 40°C) (Burt 1974).

Atrazine may be removed from terrestrial and aquatic environments by both microbial and chemical degradation. Microbial degradation occurs primarily via dealkylation to yield de-ethylated or de-isopropylated atrazine, whereas chemical hydrolysis yields hydroxyatrazine (Sheets 1970; Goswami and Green 1971; Best and Weber 1974; Hiltbold and Buchanan 1977; Khan 1978). In soils, the microbial breakdown of atrazine is of relatively minor importance compared with abiotic degradation (Best and Weber 1974; Geller 1980). A number of bacterial and fungal isolates, however, have the ability to degrade atrazine under controlled conditions. For example, atrazine was 73% de-ethylated by the fungus, *Aspergillus fumigatus*, after a 32-d incubation. Atrazine was slightly degraded in pure cultures of bacteria and fungi isolated from soils, water and activated sludge; de-ethylated and de-isopropylated atrazine accounted for approximately 3.2% of the starting material after incubation for 2 weeks in most of the pure cultures investigated. In sterile mineral salt solutions of pH 7.2, 4.4% of the atrazine was present as de-ethylated and 1.5% as de-isopropylated atrazine after 2 weeks of incubation (Geller 1980).

In soils, abiotic degradation of atrazine is influenced primarily by pH and organic matter content. In general, as the pH increases in the range of pH 4-7, atrazine persistence increases. Hydrolysis of atrazine proceeds more rapidly in soils with higher organic matter content (Armstrong *et al*. 1967). The hydrolysis of atrazine at pH 3.9 and 25°C in distilled water proceeds at a slow rate; its half-life is 309 d (Armstrong *et al*. 1967). In the presence of water-soluble polyelectrolytes, such as fulvic acid, hydrolysis may proceed at a faster rate. For example, in water of pH 2.9 and 25°C containing fulvic acid (500 mg·L^{-1}), the hydrolytic half-life was 35 d. As the pH increased to pH 7.0, however, the rate of hydrolysis significantly decreased, and the half-life was 742 d (Khan 1978). The decrease in hydrolysis of atrazine above pH 5 has been demonstrated for various soil types (Best and Weber 1974; Hiltbold and Buchanan 1977). Because the pH of soil solutions and surface waters is typically in the range of pH 5-8, and the fulvic acid content ranges from 100 to 5000 mg·kg^{-1}, atrazine could have an extended residual lifetime (Khan 1978).

The persistence of atrazine under field conditions has been investigated at a number of agricultural locales in Canada. Depending upon the quantity of atrazine applied, time of year, soil type and soil conditions, half-lives in soils of depth 0 to 6 cm can range from 20 d (Ivany *et al*. 1985) to greater than 3 months (Frank and Sirons 1985). Atrazine had a half-life of 3.0-3.6 months when applied at an average of 1.6 kg-ai·ha^{-1} to clay loam soil (32% clay, 4.8% organic matter, pH 7.1) between 1970 and 1980 in corn production areas in Ontario. Field monitoring of various soils in Ontario indicated a half-life of 2.4-3.0 months. De-ethylated atrazine (the major metabolite, indicating microbial degradation) accounted for approximately 15% of total residue after 2.5 months and 22% after 12 months. At an application of 1.1 kg-ai·ha^{-1}, approximately 0.13 μg·g^{-1} residues were found after 5 months and approximately 0.06 μg·g^{-1} after 12 months (Frank and Sirons 1979). In sandy loam soils in Prince Edward Island, atrazine, at an application of 1.13 kg-ai·ha^{-1}, had a half-life of approximately 20 d (Ivany *et al*. 1985). In a long-term study, atrazine was applied at 1.4-2.4 kg-ai·ha^{-1} 20 times between 1959 and 1978 to corn fields at the Central Experimental Farm, Ottawa. Soil concentrations in 1978 were 0.1 μg·g^{-1}; 1 year after the final application, concentrations had decreased to 0.06 μg·g^{-1} (Khan and Saidak 1981). Other studies have indicated that residue carry-over from one year to the next varies from 5 to 13% (Wu 1980); in general, carry-over is usually less than 10% in clay loam and loam soils (Smith 1982; Smith and Bubar 1984). Atrazine may, however, persist in some soils. Approximately 50% of the initially applied atrazine was found in the bound (nonextractable) fraction of soil up to 9 years after application. Dealkylated and hydroxylated atrazine, as well as the parent compound, were identified in this fraction (Capriel *et al*. 1985).

Compared with terrestrial systems, very little information is available on the persistence of atrazine in the aquatic environment. In a continuous-flow aquatic microcosm containing a 0.5-cm layer of pond sediment, water and plankton held at 22°C, no significant degradation of atrazine (at microgram per litre concentrations) was observed after 50 d (Brockway *et al*. 1984). Soon after the application of atrazine to small farm pond ecosystems, residues were identified in all compartments, although no preferential concentration occurred in any one compartment, and no biological magnification was observed (Klassen and Kadoum 1979). Bioconcentration factors of 10-83 for algae, 2-15 for snails and 3-10 for fish (species and test conditions unspecified) have been reported (Verschueren 1983).

6.3.12.7.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Agriculture Canada. 1985. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/85.

Armstrong, D.E., G. Chesters and R.F. Harris. 1967. Atrazine hydrolysis in soil. Soil Sci. Soc. Am. Proc. 31: 61-66. (Cited in Jordan *et al*. 1970.)

Best, J.A. and J.B. Weber. 1974. Disappearance of *s*-triazines as affected by soil pH using a balance-sheet approach. Weed Sci. 22: 364-373.

Brockway, D.L., P.D. Smith and F.E. Stancil. 1984. Fate and effects of atrazine in small aquatic microcosms. Bull. Environ. Contam. Toxicol. 32: 345-353.

Burkland, N. and J.A. Guth. 1976. Photodegradation of atrazine, atraton and ametryne in aqueous solution with acetone as a photosensitiser. Pestic. Sci. 7: 65-71.

Burt, G.W. 1974. Volatility of atrazine from plant, soil and glass surfaces. J. Environ. Qual. 3: 114-117.

Capriel, P., A. Haisch and S.U. Khan. 1985. Distribution and nature of bound (non-extractable) residues of atrazine in a mineral soil nine years after the herbicide application. J. Agric. Food Chem. 33: 567-569.

Davis, D.E., D.R. Roberts and H.H. Funderburk, Jr. 1963. Radiochemical assay procedures for atrazine and atrazine degradation products. Proc. South. Weed Conf. 16: 380-386. (Cited in Jordan *et al*. 1970.)

Environment Canada/Ministère de l'Environnement du Québec. 1984. Les Pesticides en Agriculture au Québec en 1982. Service de la protection de l'environnement/Service de l'assainissement agricole, Montréal, Québec. 134 pp.

Frank, R. and G.J. Sirons. 1979. Atrazine: its use in corn production and its loss to stream waters in southern Ontario, 1975-1977. Sci. Total Environ. 12: 223-239.

Frank, R. and G.J. Sirons. 1985. Dissipation of atrazine residues from soils. Bull. Environ. Contam. Toxicol. 34: 541-548.

Frank, R., G.J. Sirons, R.L. Thomas and K. McMillan. 1979. Triazine residues in suspended solids (1974-1976) and water (1977) from the mouths of Canadian streams flowing into the Great Lakes. J. Great Lakes Res. 5: 131-138.

Geller, A. 1980. Studies in the degradation of atrazine by bacteria communities enriched from various biotopes. Arch. Environ. Contam. Toxicol. 9: 289-305.

Goswami, K.P. and R.E. Green. 1971. Microbial degradation of the herbicide atrazine and its 2-hydroxy analog in submerged soils. Environ. Sci. Technol. 5: 426-429.

Hiltbold, A.E. and G.A. Buchanan.1977. Influence of soil pH in persistence of atrazine in the field. Weed Sci. 25: 515-520.

Ivany, J.A., J.M. Sadler, E.R. Kimball and K.B. McRae. 1985. Atrazine persistence and residue effects on rotation crops. Can. J. Plant Sci. 65: 363-368.

Jordan, L.J., W.J. Farmer, J.R. Goodin and B.E. Day. 1970. Volatilization and non-biological degradation of triazine herbicides *in vitro* and in soils. Residue Rev. 32: 267-286.

Kearney, P.C., T.J. Sheets and J.W. Smith. 1964. Volatility of seven *s*-triazines. Weeds 12: 83-87. (Cited in Jordan *et al*. 1970.)

Kenaga, E.E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotoxicol. Environ. Saf. 4: 26-38.

Khan, S.U. 1978. Kinetics of hydrolysis of atrazine in aqueous fulvic acid solution. Pestic. Sci. 9: 39-43.

Khan, S.U. and W.J. Saidak. 1981. Residues of atrazine and its metabolites after prolonged usage. Weed Res. 21: 9-12.

Klassen, H.E. and A.M. Kadoum. 1979. Distribution and retention of atrazine and carbofuran in farm pond ecosystems. Arch. Environ. Contam. Toxicol. 8: 345-353.

Lynch, T.R., H.E. Johnson and W.J. Adams. 1985. Impact of atrazine and hexachlorobiphenyl on the structure and function of model stream ecosystems. Environ. Toxicol. Chem. 4: 399-413.

Muir, D.C.G., J.Y. Yoo and B.E. Baker. 1978. Residues of atrazine and *N*-dealkylated atrazine in water from five agricultural watersheds in Quebec. Arch. Environ. Contam. Toxicol. 7: 221-225.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ontario Ministry of Agriculture and Food. 1984. Survey of Pesticide Use in Ontario, 1983. Economics Rep. No. 84-05. 39 pp.

Ralston, J.G. 1986. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Sheets, T.J. 1970. Persistence of triazine herbicides and related problems. Residue Rev. 32: 287-310.

Smith, A.E. 1982. Herbicides and the soil environment in Canada. Can. J. Soil Sci. 62: 433-460.

Smith, A.E. and C.J. Bubar. 1984. Persistence of triazine herbicides in Canadian soils. Canadian Pest Management Society, Proc. 31st Annu. Meet., August 20-22, Winnipeg, Manitoba.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Triplett, G.B., Jr., B.J. Conner and W.M. Edwards. 1978. Transport of atrazine and simazine in runoff from conventional and no-tillage corn. J. Environ. Qual. 7: 77-84.

U.S. EPA. 1975. Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides. U.S. Environmental Protection Agency, Washington, D.C. Prepared in cooperation with R.R. Consultants, Shawnee Mission, Kansas. Contract No. EQC-311.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Wauchope, R.D. and R.S. Myers. 1985. Adsorption-desorption kinetics of atrazine and linuron in freshwater-sediment aqueous slurries. J. Environ. Qual. 14: 132-136.

Wehtje, G.R., R.F. Spalding, O.C. Burnside, S.R. Lowry and J.R.C. Leavitt. 1983. Biological significance and fate of atrazine under aquifer conditions. Weed Sci. 31: 610-618.

Wolfe, N.L., R.G. Zepp, J.A. Gordon and R.C. Fincher. 1976. *N*-Nitrosamine formation from atrazine. Bull. Environ. Contam. Toxicol. 15: 342-347.

Worthing, C.R. (ed.). 1983. The Pesticide Manual. A World Compendium. 7th edition. The British Crop Protection Council. Lavenham Press Ltd., Lavenham, U.K. p. 23.

Wu, T. 1980. Dissipation of the herbicides atrazine and alachlor in a Maryland corn field. J. Environ. Qual. 9: 459-465.

6.3.12.8 Miscellaneous Compounds

6.3.12.8.1 Acrolein

6.3.12.8.1.1 Uses and Production

Acrolein is used for the control of aquatic weeds, for the control of molluscs in recirculating process water systems and for slime control in the paper industry. It is also used to protect liquid fuels from the action of microorganisms, in leather tanning and as an intermediate in the chemical industry (U.S. EPA 1980).

Worldwide production of acrolein in 1975 was approximately 54×10^3 t (U.S. EPA 1980). Approximately 227×10^6 kg are produced annually (Beauchamp *et al.* 1985).

Magnachem Ltd. of Calgary is the only agent in Canada that markets acrolein under the trade names Magnicide H and Magnicide B. Magnicide H is used to control submerged and floating weeds in irrigation canals. Magnicide B is used to control bacteria and fungi in oilfield water (water kept to inject into a drill bit to clean off mud). Both products have the same formulation (92% acrolein as active ingredient). No production of acrolein is carried out in Canada, and import data are unavailable (Stewart 1985).

Additional names for acrolein that are used in Canada include 2-propenal; acrylaldehyde; Aqualin; and Magnicide (Agriculture Canada 1984).

6.3.12.8.1.2 Sources and Pathways for Entering the Aquatic Environment

Acrolein enters the aquatic environment through its use as an aquatic herbicide, from industrial discharges and from the chlorination of organic compounds in wastewaters. The primary source of acrolein in air is the partial combustion of organic material. Forest and urban fires are major contributors, along with exhaust emissions from internal combustion engines and tobacco smoke (Beauchamp *et al.* 1985). The amount of acrolein reaching the aquatic environment from atmospheric deposition is unknown.

6.3.12.8.1.3 Environmental Concentrations

Liquid effluents from some industrial plants have been found to contain several aldehydes, including acrolein. In addition, acrolein has been detected in the effluents from paper mills (Beauchamp *et al.* 1985). Municipal effluents in Dayton, Ohio, contained acrolein in 6 of 11 samples, with concentrations ranging from 20 to 200 $\mu g \cdot L^{-1}$ (U.S. EPA 1977). No Canadian data on acrolein concentrations are available.

6.3.12.8.1.4 Forms and Fate in the Aquatic Environment

Acrolein, CH_2CHCHO, is a colourless to yellowish liquid with a boiling point of 52.5°C, a vapour pressure of 29 kPa at 20°C and a water solubility of 20.8% at 20°C (Verschueren 1983). The calculated octanol/water partition coefficient is 0.8 (Radding *et al.* 1977).

One field observation has indicated that acrolein may persist in running water over significant distances. An initial concentration of 100 $\mu g \cdot L^{-1}$ acrolein (added to a canal) was dissipated as a function of distance with 90, 50 and 30 $\mu g \cdot L^{-1}$ being detected 8, 16 and 32 km downstream (Bartley and Gangstad 1974). Other field studies, however, have indicated a rapid loss of acrolein from the water column if initial acrolein concentrations are low ($<$2-3 $mg \cdot L^{-1}$) (Bowmer and Higgins 1976).

The major fate of acrolein appears to be reversible hydrolysis to β-hydroxypropionaldehyde (Bowmer and Higgins 1976), although little reliable information is available to assess the fate of acrolein in the aquatic environment (U.S. EPA 1979).

No information is available on the photolysis of acrolein in aqueous systems; studies of the gas-phase photolysis of acrolein suggest that it would be slowly degraded in the atmosphere (Coomber and Pitts 1969). It has been predicted that oxidation would occur only very slowly in the aquatic environment. Half-lives of approximately 6 years and more than 20 years have been estimated for oxidation with singlet oxygen (Zepp *et al.* 1977) and alkylperoxyl radicals (Mill 1979), respectively. There is conflicting information regarding the importance of volatilization in the removal of acrolein from the water column. Volatilization has been suggested in one field study (Bowmer and Higgins 1976), but discounted in another (U.S. EPA 1979).

No reliable information is available to assess the importance of sorption in the removal of acrolein from the water column. Sorption, along with volatilization, was suggested as a primary process in one field study (Bowmer and Higgins 1976); the high water solubility and low partition coefficient of acrolein suggest, however, that sorption does not play a significant role in the aquatic environment (U.S. EPA 1979).

Biodegradation readily occurs during sewage and activated sludge treatment (Wierzbicki and Wojcik 1965; Brink 1976); the evidence for biodegradation in the aquatic environment, however, is ambiguous (U.S. EPA 1979).

Bluegill sunfish (*Lepomis macrochirus*), exposed for 28 d to 13 $\mu g \cdot L^{-1}$ acrolein, bioconcentrated acrolein 344 times (whole body) (U.S. EPA 1978, 1980). The biological half-life was found to be greater than 7 d (Barrows *et al.* 1980).

6.3.12.8.1.5 References

Agriculture Canada. 1984. Compendium of Pest Control Products Registered in Canada. Registered Pest Control Products. Volume Code: RP. Pesticides Division, Plant Health and Plant Products Directorate, Ottawa. Publ. No. 1654 RP/84.

Barrows, M.E., S.R. Petrocelli, K.J. Macek and J.J. Carroll. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 379-392.

Bartley, T. and E.O. Gangstad. 1974. Environmental aspects of aquatic plant control. ASCE J. Irrig. Drain. Div. 100: 231-244. (Cited in U.S. EPA 1979.)

Beauchamp, R.O., Jr., D.A. Andjelkovich, A.D. Kligerman, K.T. Morgan and H. d'A. Heck. 1985. A critical review of the literature on acrolein toxicity. CRC Crit. Rev. Toxicol. 14: 309-380.

Bowmer, K.H. and M.L. Higgins. 1976. Some aspects of the persistence and fate of acrolein herbicide in water. Arch. Environ. Contam. Toxicol. 5: 87-96.

Brink, R.H., Jr. 1976. Studies with chlorophenols, acrolein, dithiocarbamates and dibromonitrilopropionamide in bench-scale biodegradation units. *In* Proc. 3rd Int. Biodegradation Symp, 1975, London. Applied Science Publ. Ltd. pp. 785-791. (Cited in U.S. EPA 1979.)

Coomber, J.W. and J.N. Pitts, Jr. 1969. Molecular structure and photochemical reactivity. XII. The vapor-phase photochemistry of acrolein at 3130 Å. J. Am. Chem. Soc. 91: 547-550.

Mill, T. 1979. Structure Reactivity Correlations for Environmental Reactions. U.S. Environmental Protection Agency, Washington, D.C. Final Report. EPA-560/11-79-012.

Radding, S.B., D.H. Liu, H.L. Johnson and T. Mill. 1977. Review of the Environmental Fate of Selected Chemicals. U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-77-003. (Cited in U.S. EPA 1979.)

Stewart, M. 1985. Personal communication. Pesticides Division, Agriculture Canada, Ottawa.

U.S. EPA. 1977. Survey of Two Municipal Wastewater Treatment Plants for Toxic Substances. Wastewater Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. (Cited in U.S. EPA 1980.)

U.S. EPA. 1978. In-depth Studies on Health and Environmental Impacts of Selected Water Pollutants. U.S. Environmental Protection Agency, Washington, D.C. Contract No. 68-01-4646. (Cited in U.S. EPA 1980.)

U.S. EPA. 1979. Acrolein. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 20-1 to 20-11.

U.S. EPA. 1980. Ambient Water Quality Criteria for Acrolein. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA 440/5-80-016.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. 1310 pp.

Wierzbicki, T. and O. Wojcik. 1965. Preliminary trials on the decomposition of acrolein, allyl alcohol and glycerol by activated sludge. Zesz. Nauk. Politech. Slask. Inz. Sanit. 8: 173-185. (Cited in U.S. EPA 1979.)

Zepp, R.G., N.L. Wolfe, G.L. Baughman and R.C. Hollis. 1977. Singlet oxygen in natural water. Nature (London) 267: 421-423.

Table 6-144. Amount of Phthalate Esters Used as Plasticizers in Polyvinyl Chloride Products in 1981 and 1982

	Amount (t)	
PVC product	1981	1982
PVC film	2 200	1900
PVC sheet	11 500	9500
PVC wire and cable insulation	10 500	9500
PVC extrusion	3 700	3200
Vinyl flooring	9 800	8200
Vinyl plastisols	1 900	1500
Footwear	2 600	2200

Source: Bovet 1984.

6.3.13 Phthalate Esters

6.3.13.1 Uses and Production

Phthalate esters represent a large group of chemicals widely used as plasticizers in polyvinyl chloride (PVC) resins, adhesives and cellulose film coating. Other applications are found in cosmetics, rubbing alcohol, insect repellant, insecticides, tablet coating and solid rocket propellants (Pierce *et al.* 1980; Environment Canada 1983). Only the amounts of phthalate esters used as plasticizers for polyvinyl chloride products in Canada are known; these are presented in Table 6-144 (Bovet 1984).

Among the most common phthalate esters are dimethyl (DMP), diethyl (DEP), di-*n*-butyl (DBP), di-(2-ethylhexyl) (DEHP), di-*n*-hexyl (DHP), di-*iso*-decyl, di-*iso*-octyl (DOP) and *n*-butylbenzyl phthalate (Pierce *et al.* 1980; Environment Canada 1983). Oftentimes DEHP is incorrectly named as DOP, resulting in confusion in the literature (Pierce *et al.* 1980).

Since the early 1980's, 90% of the phthalate esters consumed in Canada were manufactured in this country (Ontario and Quebec only), and the remaining 10% were imported. Between 1979 and 1983, an average of 40 000 t of phthalate esters were used in Canada and approximately 4000 t·a^{-1}

Table 6-145. Production, Consumption, Importation and Exportation of Dioctyl Phthalate, 2-Ethylhexanol and Phthalate Anhydride in Canada

		Amount (t)			
Compound	Year	Production	Consumption	Importation	Exportation
Dioctyl phthalate (di(2-ethylhexyl) phthalate)	1982	13 800	14 000	200	0
	1983	16 600	17 500	900	0
	1984	16 800	18 000	1200	0
2-Ethylhexanol	1982	41 000	41 000	120	
	1983	46 000	46 000	120	
Phthalate anhydride	1982	18 000	21 000	3900	1000
	1983	22 350	26 000	4500	500

Sources: CORPUS Information Services 1983, 1984; Bovet 1984.

were imported (Bovet 1984). Butylbenzyl phthalate accounted for 60% of the imports, followed by dioctyl phthalate (13%), di-*iso*-decyl phthalate (6%) and about 10 other phthalate esters which made up the remaining 21% of imports.

The main phthalate ester produced in Canada is dioctyl phthalate, production of which has been estimated at 17 000 $t{\cdot}a^{-1}$. Di-*iso*-decyl phthalate, diundecyl phthalate and linear phthalate mixtures are also important phthalate esters manufactured in Canada. Of the 16 phthalate esters produced in Canada, production data are available only for dioctyl phthalate. Canadian production, importation and consumption for dioctyl phthalate and its raw materials, 2-ethylhexanol and phthalic anhydride, are presented in Table 6-145 (CORPUS Information Services 1983, 1984; Bovet 1984). Importation data for seven of the other Canadian-produced phthalate esters are presented in Table 6-146 (Statistics Canada 1984). There were no imports of the remaining phthalate esters produced in Canada, which include di-*iso*-nonyl phthalate, di-*iso*-octyl phthalate, dimethylcyclohexyl phthalate, ditridecyl phthalate, diundecyl phthalate and dinonyl phthalate (Bovet 1984).

Phthalate esters are included in Category II of the Environmental Contaminants Act, List of Priority Chemicals. Because of their wide use in Canada, phthalate esters are being investigated to determine the nature and extent of the danger to human health or the environment which these compounds may pose and to determine the appropriate means to alleviate the potential danger (Environment Canada 1985).

6.3.13.2 Sources and Pathways for Entering the Aquatic Environment

Because of the large production and many different uses of phthalate esters, these compounds can be released to the environment from a variety of sources. For example, PVC manufacturing plants, textile and paper mill industries, landfill sites and municipal incinerators can all contribute to the presence of phthalate esters in the aquatic environment. Nonplasticizer applications represent only a small portion (approximately 1%) of the total demand. However, the phthalate esters used in their manufacture can be readily released to the aquatic environment, as they are not incorporated into the matrix of a polymeric structure such as polyvinyl chloride (Pierce *et al.* 1980).

Phthalate esters were detected in the total effluent of five Canadian organic chemical plants surveyed in early 1985. The concentration ranges are presented in Table 6-147 (Sigma Resource Consultants Ltd. 1985). In a survey of municipal and industrial discharges in Cornwall, Ontario, phthalate esters were detected in the final effluent, and concentration ranges are presented in Table 6-148 (Environment Canada 1984). Phthalate esters were observed in the final effluent of various petrochemical plants along the St. Clair River, and their concentrations are presented in Table 6-149 (Munro *et al.* 1985).

Table 6-146. Importation Data on 7 of the 16 Phthalate Esters into Canada

	Amount (t)	
Compound	1981	1982
Butylbenzyl phthalate	1504	2131
Butyloctyl phthalate	2	3
Dibutyl phthalate	45	76
Dicyclohexyl phthalate	19	19
Di-*iso*-decyl phthalate	101	168
Dimethyl phthalate	107	86
Di(*n*-octyl, *n*-decyl) phthalate	1	21

Source: Statistics Canada 1984.

Estimates of the quantities of phthalate esters released to the Canadian environment during 1973 as a result of production and processing ranged from 720 to 1600 t, whereas the quantities released from use and disposal activities were approximately 3800 t (Health and Welfare Canada 1980a).

6.3.13.3 Environmental Concentrations

Only some phthalate esters are frequently found in the environment. Phthalate esters have been found in water samples taken from Lake Superior (<1-1.4 $\mu g{\cdot}L^{-1}$ as DEHP), Lake Huron (0.04 $ng{\cdot}L^{-1}$ as DBP), Lake Erie and Lake Ontario (Health and Welfare Canada 1980a, b). Sampling results for phthalate esters are not reported in NAQUADAT (1985). Five phthalate esters were detected in the surface waters of the St. Clair River, and the results are presented in Table 6-150 (Munro *et al.* 1985).

DEHP and DBP at concentrations of 100-300 $\mu g{\cdot}kg^{-1}$ have been found in sediments from certain regions of Lake Superior and Lake Huron (Health and Welfare Canada 1980b). DEHP was found in North Atlantic waters at concentrations ranging from 0.1 to 6.3 $ng{\cdot}L^{-1}$ (Health and Welfare Canada 1980a).

Several phthalate esters have been identified in air samples collected near a municipal incinerator in Hamilton, Ontario.

Table 6-147. Concentration Ranges for Various Phthalate Esters Detected in Total Effluents of Five Canadian Organic Chemical Plants

Compound	Detection limit ($mg\cdot L^{-1}$)	Concentration range ($mg\cdot L^{-1}$)
Dimethyl phthalate	0.01	ND[1]-0.11
Diethyl phthalate	0.01	ND-0.56
Di-*n*-butyl phthalate	0.001	ND-0.061
Butylbenzyl phthalate	0.001	ND-0.022
Bis(2-ethylhexyl) phthalate	0.001	0.002-0.048
Di-*n*-octyl phthalate	0.001	ND

[1] ND = not detected.

Source: Sigma Resource Consultants Ltd. 1985.

Table 6-148. Concentration Ranges for Various Phthalate Esters Detected in the Final Effluent from Industrial and Municipal Plants Discharging into the St. Lawrence River at Cornwall

Compound	Gross loadings ($kg\cdot d^{-1}$)	Concentration range ($\mu g\cdot L^{-1}$)	Detection frequency (%)
Butylbenzyl phthalate	0	ND[1]	0
Di-*n*-butyl phthalate	3.59	ND-94	39
Diethyl phthalate	0	ND	0
Dimethyl phthalate	0	ND	0
Di-*n*-octyl phthalate	0.093	ND-10	17

[1] ND = not detected.

Source: Environment Canada 1984.

Table 6-149. Concentration Ranges for Various Phthalate Esters Detected in the Final Effluent of Petrochemical Plants Along the St. Clair River

Compound	Concentration range[1] ($\mu g\cdot L^{-1}$)	Number of samples	Number of samples with detectable concentrations
Dimethyl phthalate	1-100	21	8
	100-1000	2	2
Di-*n*-butyl phthalate	1-100	28	13
Butylbenzyl phthalate	1-10	7	1
Bis(2-ethylhexyl) phthalate	1-100	34	9
Di-*n*-octyl phthalate	D[1]	10	2

[1] D = detected.

Source: Munro *et al.* 1985.

Table 6-150. Concentration Ranges for Five Phthalate Esters Detected in the Surface Waters of the St. Clair River

Compound	Concentration range[1] ($\mu g\cdot L^{-1}$)	Number of samples	Number of samples with detectable concentrations
Dimethyl phthalate	1-10	9	6
Di-*n*-butyl phthalate	1-100	9	6
Butylbenzyl phthalate	D[1]	7	4
Bis(2-ethylhexyl) phthalate	1-100	47	20
Di-*n*-octyl phthalate	1-10	8	8

[1] D = detected.

Source: Munro *et al.* 1985.

The concentrations of DBP and DEHP were 0.7 and 0.3 $\mu g\cdot m^{-3}$, respectively (U.S. EPA 1980).

Phthalate ester concentrations found in Great Lakes fish, notably from Lake Superior, ranged from 5000 to 20 000 $\mu g\cdot kg^{-1}$ (Health and Welfare Canada 1980b). DBP levels in fish available to Canadian consumers ranged between nondetectable and 78 $\mu g\cdot kg^{-1}$, and DEHP levels ranged from nondetectable to 160 $\mu g\cdot kg^{-1}$. Some fish samples available to Canadian consumers contained phthalate esters at concentrations of 240 $\mu g\cdot kg^{-1}$ on a wet-weight basis (U.S. EPA 1980).

6.3.13.4 Forms and Fate in the Aquatic Environment

Phthalate esters are the diesters of 1,2-benzenedicarboxylic acid (*o*-phthalic acid). 1,3- and 1,4-diesters (*m*- and *p*-phthalate esters) are termed *iso*-phthalate and terephthalate esters, respectively (Pierce *et al.* 1980). Production and use of the *m*- and *p*-phthalate esters, however, do not compare with those of the *o*-isomers. Phthalate esters are usually colourless, odourless, viscous liquids with high boiling points and low vapour pressures (Table 6-151) (U.S. EPA 1979; Pierce *et al.* 1980; Environment Canada 1983; Pierson *et al.* 1984). In general, vapour pressure decreases with increasing length of the alcohol side chain of the ester. Among phthalate esters with isomeric side chains, vapour pressure tends to increase with increasing chain branching (Pierce *et al.* 1980). Water solubility is low and, as with vapour pressure, is dependent upon the length and configuration of the side chains. There is no clear relationship, however, between solubility and side-chain configuration.

Although insoluble in pure water, phthalate esters may be transported in the aquatic environment in solubilized form by fulvic and humic acids. This solubilization has been found to be pH-dependent, with 25% more phthalate ester complexation with fulvic acid at pH 2.45 than at pH 7 (Ogner and Schnitzer 1970; Matsuda and Schnitzer 1971). The primary aquatic transport mechanisms for phthalate esters are most probably complexation with humic substances and sorption by particulate matter and biota. Depending upon specific conditions in aquatic ecosystems, bioaccumulation and biodegradation will also be significant (U.S. EPA 1979; Pierce *et al.* 1980).

Calculated log octanol/water partition coefficients for various phthalate esters range from 1.5 to 4, indicating some potential for uptake by organic material, at least for the longer-chain phthalate esters (Table 6-151) (U.S. EPA 1979; Pierce *et al.* 1980). Field surveys have indicated a higher concentration of phthalate esters in sediments than in waters, suggesting some preferential concentration onto particulate matter (Pierce *et al.* 1980).

Photolysis and oxidation are not expected to be significant processes in the aquatic environment (U.S. EPA 1979; Pierce *et al.* 1980). Likewise, chemical hydrolysis is not considered significant because hydrolytic half-lives are in the order of years (Tomita *et al.* 1977).

Numerous organisms, including bacteria, fungi, invertebrates and vertebrates, are capable of metabolizing phthalate esters under a number of different environmental conditions.

Table 6-151. Physical-chemical Properties of Some Phthalate Esters

Compound	Molecular weight	Side-chain configuration	Specific gravity at 25°C	Melting point (°C)	Boiling point (°C) (101 kPa)	Vapour pressure (kPa)	Water solubility (mg·L^{-1} (20°C))	Solvent solubility	Octanol/water partition coefficient (log P_{ow})
Short-chain									
Dimethyl phthalate (DMP)	194.2	$-CH_3$ $-CH_3$	1.188-1.192	0.0 (freezes)	147 (1.3 kPa) 282	1.5×10^{-4}	5000	Insoluble in petroleum oils; soluble in all other common organic solvents and oils	1.5
Diethyl phthalate (DEP)	222.3	$-CH_2CH_3$ $-CH_2CH_3$	1.115-1.119	-40.5	158 (1.3 kPa) 296	5.0×10^{-5}	1000	Soluble in all common organic solvents and oils	1.8
Di-*n*-butyl phthalate (DnBP)	278.4	$-(CH_2)_3CH_3$ $-(CH_2)_3CH_3$	1.044-1.048	-35	192 (1.3 kPa) 340	1.9×10^{-6}	4500 (25°C)	Soluble in all common organic solvents and oils	2.2
Di-*iso*-butyl phthalate (DiBP)	278.4	$-CH_2CH(CH_3)_2$ $-CH_2CH(CH_3)_2$	1.040	-50	327	–	100	–	–
Long-chain									
n-Butylbenzyl phthalate (nBBP)	298.4	$-(CH_2)_3CH_3$ $-CH_2(C_6H_4)$	–	–	–	–	–	–	–
Dicyclohexyl phthalate (DCHP)	330.4	$-C_6H_5$ $-C_6H_5$	1.29	63.0	231 (1.3 kPa)	6.0×10^{-8}	<100 (25°C)	Soluble in acetone, *n*-butanol, carbon tetrachloride, cyclohexanone, ethyl acetate, ethyl ether, toluene	3-4
n-Butyl-*n*-octyl phthalate (nBnOP)	334.5	$-(CH_2)_3CH_3$ $-(CH_2)_7CH_3$	1.001	-50	340 (98.6 kPa) 340	–	–	–	–
n-Butyl-*n*-decyl phthalate (nBnDP)	362.6	$-(CH_2)_3CH_3$ $-(CH_2)_9CH_3$	–	–	–	–	–	–	–
Di-*n*-octyl phthalate (DnOP)	390.6	$-(CH_2)_7CH_3$ $-(CH_2)_7CH_3$	0.978	-25	220	$<3 \times 10^{-2}$ (150°C)	–	–	3-4
Di-(2-ethylhexyl) phthalate (DEHP)	390.6	$-CH_2CH(CH_2CH_3)(CH_2)_3CH_3$ $-CH_2CH(CH_2CH_3)(CH_2)_3CH_3$	0.980-0.985	-50	236 (1.3 kPa) 387 (0.7 kPa)	2.1×10^{-8}	<50 (25°C)	Miscible with most common solvents	3-4
Di-*iso*-octyl phthalate (DiOP)	390.6	$-(CH_2)_4CH(CH_3)_2$ $-(CH_2)_4CH(CH_3)_2$	0.981	-4	239 (0.7 kPa)	1.3×10^{-1} (200°C)	–	–	3-4
n-Octyl-*n*-decyl phthalate (nOnDP)	418.7	$-(CH_2)_7CH_3$ $-(CH_2)_9CH_3$	0.970	-28	250 (0.7 kPa)	–	–	–	3-4
Di-*iso*-decyl phthalate (DiDP)	446.7	$-(CH_2)_7CH(CH_3)_2$ $-(CH_2)_7CH(CH_3)_2$	0.963-0.969	-48	256 (1.3 kPa)	4.7×10^{-10}	<50 (25°C)	Limited solubility in glycerine, glycols and some amines; soluble in most other organic liquids	3-4
Ditridecyl phthalate (DTDP)	530.9	$-(CH_2)_{11}CH_3$ $-(CH_2)_{11}CH_3$	1.054	-37	235 (0.5 kPa)	–	–	–	3-4

Sources: U.S. EPA 1979; Pierce *et al.* 1980.

Although numerous studies have examined metabolic pathways, few have reported reliable metabolic rates. Hence, it is difficult to determine the environmental significance of phthalate ester metabolism in the aquatic environment (U.S. EPA 1979; Pierce *et al.* 1980; Pierson *et al.* 1984).

Several species of bacteria are able to completely degrade phthalate esters. Aerobic conditions appear to be necessary for bacterial metabolism. For example, within 24 h, 46% of the ^{14}C-di-*n*-butyl phthalate added to a freshwater pond hydrosoil was degraded aerobically; 98% was degraded in 5 d. However, under anaerobic conditions, only 61% was degraded in 5 d. Similarly, di-(2-ethylhexyl) phthalate was 50% degraded in 14 d under aerobic conditions, but not degraded at all after 30 d under anaerobic conditions (Johnson and Lulves 1975). Temperature also plays an important role. Di-*n*-octyl phthalate and di-(2-ethylhexyl) phthalate were degraded at 22 and 32°C, but not at 4 and 10°C (Mathur 1974). Microbial degradation is shown to vary with the specific ester; in general, degradation is less rapid for phthalate esters containing large, branched side chains (Saeger and Tucker 1976).

Although many freshwater invertebrates can degrade phthalate esters, the type and degree of metabolism vary with the organism (Wofford *et al.* 1981). Degradation appears to be slower in invertebrates than in fish (Sanborn *et al.* 1975; Södergren 1982).

Several fish species, including channel catfish (*Ictalurus punctatus*), rainbow trout (*Salmo gairdneri*) and fathead minnow (*Pimephales promelas*), may degrade phthalate esters (Stalling *et al.* 1973; Melancon and Lech 1976; Mehrle and Mayer 1976; Melancon *et al.* 1977; Binder and Stegeman 1980; Stegeman and Chevion 1980). The rate of degradation is relatively rapid. For example, more than 85% of di-(2-ethylhexyl) phthalate was degraded by various fishes within 24 h (Stalling *et al.* 1973; Melancon and Lech 1976). In general, short and partially oxidized alkyl phthalate esters are more easily degraded than branched-chain phthalate esters, such as di-(2-ethylhexyl) phthalate (Saeger and Tucker 1976; Mayer 1976).

Phthalate esters have been identified in aquatic biota, and information available from laboratory and field studies indicates that a variety of organisms may take up and accumulate them. The majority of bioaccumulation data refer to di-(2-ethylhexyl) phthalate. Much of the bioaccumulation data for phthalate esters must be interpreted with care because of differences in experimental protocol (e.g. nominal vs. measured concentration, dry weight vs. wet weight of test organisms, use of supersaturated solutions, lack of attainment of equilibrium); in addition, different organisms and life stages within the same species have often been used (Pierce *et al.* 1980).

Studies on the accumulation of phthalate esters by freshwater invertebrates have been contradictory, with bioconcentration factors differing by at least an order of magnitude for the same test organism (Pierce *et al.* 1980; Pierson *et al.* 1984). In general, freshwater invertebrates concentrated phthalate esters from 10^2 to 10^4 times the concentration found in water. For example, *Daphnia magna* concentrated di-(2-ethylhexyl) phthalate (at microgram per litre concentrations) to equilibrium levels 166 (Brown and Thompson 1982) to 518 (Macek *et al.* 1979) those found in water during long-term laboratory exposures.

Although freshwater invertebrates may metabolize phthalate esters, the rate and extent of such degradation are less than those for fishes (Pierce *et al.* 1980; Pierson *et al.* 1984). In general, most freshwater fishes accumulate phthalate esters during continuous exposure at concentrations approximately 100-500 times the concentration present in water (Pierson *et al.* 1984). Bioconcentration factors of 155-747 at equilibrium and 25°C were recorded for di-(2-ethylhexyl) phthalate (1-60 $\mu g \cdot L^{-1}$) exposures of fathead minnows (*Pimephales promelas*) (Mayer 1976). At low concentrations ($<5\ \mu g \cdot L^{-1}$), equilibrium body concentrations in fathead minnows were approximately 500 times the concentration in water (Pierce *et al.* 1980). Bluegills (*Lepomis macrochirus*) exposed to 1 $\mu g \cdot L^{-1}$ di-(2-ethylhexyl) phthalate for 35 d had a bioconcentration factor of 112 (Macek *et al.* 1979). Exposure to 9-10 $\mu g \cdot L^{-1}$ dimethyl, diethyl and butylbenzyl phthalate resulted in bioconcentration factors of 57, 117 and 776, respectively, for bluegills (Veith and Austin 1976).

Once exposure discontinues, depuration from most fishes appears to be rapid. For example, di-(2-ethylhexyl) phthalate was excreted from bluegills with a half-life of 9.7-21.6 d (Mayer 1976), whereas the monoester, the primary metabolite of the diester, was excreted more rapidly, with a half-life of 5.7 d (Pierce *et al.* 1980). Although aquatic organisms may accumulate phthalate esters under conditions of continuous exposure, it is unlikely that biomagnification in aquatic food webs will be significant, because efficient degradation and excretion by fish occur (Pierce *et al.* 1980).

6.3.13.5 References

Binder, R.L. and J.J. Stegeman. 1980. Induction of aryl hydrocarbon hydroxylase activity in embryos of an estuarine fish. Biochem. Pharmacol. 29: 949-951.

Bovet, Y. 1984. Report on the Canadian Market for Phthalic Acid Esters (PAE) from 1979 to 1983. Draft Report. Commercial Chemicals Branch, Environment Canada, Ottawa.

Brown, D. and R.S. Thompson. 1982. Phthalates and the aquatic environment: Part 1. The effects of di-2-ethylhexyl phthalate (DEHP) and di-isodecyl phthalate (DIDP) in the reproduction of *Daphnia magna* and observations on their bioconcentration. Chemosphere 11: 417-426.

CORPUS Information Services. 1983. Phthalic anhydride (phthalic acid anhydride). CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1984. Di(2-ethylhexyl) phthalate [Di-octyl phthalate, DEHP, DOP]. A Report Prepared for Commercial Chemicals Branch, Environment Canada, Ottawa.

Environment Canada. 1983. Phthalate acid esters. *In* Guidelines for Surface Water Quality. Vol. 2. Organic Chemical Substances. Water Quality Branch, Inland Waters Directorate, Ottawa.

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Environment Canada. 1985. Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa.

Health and Welfare Canada. 1980a. Phthalate Acid Esters. Environmental Health Directorate Publ. No. 80-EHD-62. 137 pp.

Health and Welfare Canada. 1980b. Phthalate acid esters. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 489-503.

Johnson, B.T. and W. Luives. 1975. Biodegradation of di-*n*-butyl phthalate and di-2-ethylhexyl phthalate in freshwater hydrosoil. J. Fish. Res. Board Can. 32: 333-339.

Macek, K.J., S.R. Petrocelli and B.H. Sleight, III. 1979. Considerations in assessing the potential for, and significance of, biomagnification of chemical residues in aquatic food chains. *In* Proc. 2nd Annu. Symp. on Aquatic Toxicology. ASTM STP 667. L.L. Marking and R.A. Kimerle (eds.). Am. Soc. Test. Mater. Cleveland, Ohio. pp. 251-268.

Mathur, S.P. 1974. Phthalate esters in the environment: pollutants or natural products? J. Environ. Qual. 3: 189-197.

Matsuda, K. and M. Schnitzer. 1971. Reactions between fulvic acid, a soil humic material and dialkyl phthalates. Bull. Environ. Contam. Toxicol. 6: 200-204.

Mayer, F.L. 1976. Residue dynamics of di-(2-ethylhexyl) phthalate in fathead minnows (*Pimephales promelas*). J. Fish. Res. Board Can. 33: 2610-2613.

Mehrle, P.M. and F.L. Mayer. 1976. Di-2-ethylhexyl phthalate: Residue dynamics and biological effects in rainbow trout and fathead minnows. *In* Proc. Univ. Missouri Annu. Conf. on Trace Substances in Environmental Health – X. D.D. Hemphill (ed.). June 8-10, 1976. Columbia, Missouri. pp. 519-524.

Melancon, M.J., Jr. and J.J. Lech. 1976. Distribution and biliary excretion products of di-(2-ethylhexyl) phthalate in rainbow trout. Drug Metab. Dispos. 4: 112-118. (Cited in Pierce *et al.* 1980.)

Melancon, M.J., Jr., J. Saybolt and J.J. Lech. 1977. Effect of piperonyl butoxide on disposition of di-(2-ethylhexyl) phthalate by rainbow trout. Xenobiotica 7: 633-640.

Munro, J.R., M.G. Foster, T. Pawson, A. Stelzig, T. Tseng and L. King. 1985. St. Clair River Point Source Survey, 1979-1980. Ontario Ministry of the Environment/Environment Canada, Toronto/Ottawa, Ontario. 194 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Ogner, G. and M. Schnitzer. 1970. Humic substances fulvic-acid-dialkyl phthalate complexes and their role in pollution. Science 170: 317-318.

Pierce, R.C., S.P. Mathur, D.T. Williams and M.J. Boddington. 1980. Phthalate Esters in the Aquatic Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 17583. 108 pp.

Pierson, K.B., B.D. Ross and R.E. Nakatani. 1984. Review: The Effects and Occurrence of Phthalate Esters in Aquatic Organisms and Sediments. U.S. Army Corps of Engineers, Seattle, Washington.

Saeger, V.W. and E.S. Tucker. 1976. Biodegradation of phthalic acid esters in river water and activated sludge. Appl. Environ. Microbiol. 31: 29-34.

Sanborn, J.R., R.L. Metcalf, C.-C. Yu and P.-Y. Lu. 1975. Plasticizers in the environment: the fate of di-*n*-octyl phthalate (DOP) in two model ecosystems and uptake and metabolism of DOP by aquatic organisms. Arch. Environ. Contam. Toxicol. 3: 244-255.

Sigma Resource Consultants Ltd. 1985. Study of the Characterization of Wastes and Discharges from Selected Organic Chemical Plants. Draft report. Contracted by the Environmental Protection Service, Environment Canada, Ottawa.

Södergren, A. 1982. Significance of interfaces in the distribution and metabolism of di-2-ethylhexyl phthalate in an aquatic laboratory model ecosystem. Environ. Pollut. (Ser. A) 27: 263-274.

Stalling, D.L., J.W. Hogan and J.L. Johnson. 1973. Phthalate ester residues – their metabolism and analysis in fish. Environ. Health Perspect. 3: 159-173. (Cited in Pierce *et al.* 1980.)

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Stegeman, J.J. and M. Chevion. 1980. Six differences in cytochrome P-450 and mixed function oxygenase activity in gonadally mature trout. Biochem. Pharmacol. 29: 553-558.

Tomita, A., N. Ebina and Y. Tamai. 1977. Base-catalyzed ester hydrolysis in a toluene-water system. J. Am. Chem. Soc. 99: 5725-5728.

U.S. EPA. 1979. Phthalate esters. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, and Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 94-1 to 94-28.

U.S. EPA. 1980. Ambient Water Quality Criteria for Phthalate Esters. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-067.

Veith, G.D. and N.M. Austin. 1976. Detection and isolation of bioaccumulable chemicals in complex effluents. *In* Identification and Analysis of Organic Pollutants in Water. L.H. Keith (ed.). Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. pp. 297-302.

Wofford, H.W., C.D. Wilsey, G.S. Neff, C.S. Giam and J.M. Neff. 1981. Bioaccumulation and metabolism of phthalate esters by oysters, brown shrimp and sheepshead minnows. Ecotoxicol. Environ. Saf. 5: 202-210.

6.3.14 Polyaromatic Compounds

6.3.14.1 Polycyclic Aromatic Hydrocarbons (PAHs)

6.3.14.1.1 Uses and Production

Polycyclic aromatic hydrocarbons (PAHs) are not purposely produced, but are formed by the incomplete/inefficient combustion of organic material, diagenesis and biosynthesis. Although there is a natural background of PAHs resulting from forest fires, volcanic activity, diagenesis and possibly production by some plants and microorganisms, a significant fraction of the PAHs present in the environment is the result of anthropogenic activities (Seuss 1976; NRCC 1983). Some compounds, such as perylene, phenanthrene homologs, retene and pimanthrene and tetra- and pentacyclic PAHs derived from pentacyclic triterpenes, may be formed in anaerobic sediments (Wakeham *et al.* 1980).

6.3.14.1.2 Sources and Pathways for Entering the Aquatic Environment

PAHs are generated by processes that involve the incomplete combustion of organic material. They are thus produced in the burning of fuels and refuse, and from thermal power stations and internal combustion engines (NRCC 1983). Cigarette smoking is thought to be a significant route of personal exposure, and various methods of cooking (especially smoking and frying) also contribute significant amounts (NRCC 1983).

Atmospheric deposition is believed to be a significant route of entry of PAHs into the aquatic environment, and is responsible for much of the background concentration of PAHs. Water- and land-based discharges may also contribute significant amounts of PAHs in specific locales (NRCC 1983). There are currently few quantitative data on the entry of PAHs into the aquatic environment from the atmosphere. PAHs were found to be deposited uniformly in the northeastern United States at sites distant from identifiable sources at a flux of 0.8-3 ng·cm^{-2}·a^{-1}. However, at sites closer to urban areas, the atmospheric flux was 35 ng·cm^{-2}·a^{-1} (average). The higher flux was believed to be the result of the combined input from atmospheric deposition and surface runoff (Gschwend and Hites 1981; Hites and Gschwend 1982). The total PAH input to the Great Lakes was estimated at approximately 484 t·a^{-1}. Benzo[a]pyrene input was estimated at approximately 24 t·a^{-1} (Eisenreich *et al.* 1981). It has been estimated that the global atmospheric input to the world's oceans approximates 34 000 t·a^{-1} for total PAHs and 1700 t·a^{-1} for benzo[a]pyrene (NRCC 1983).

Materials containing PAHs may directly enter the aquatic environment via the release of crude oil and petroleum products during exploration, production, transport and natural seepage, and the release of PAHs from materials used in water, such as creosoted pilings, piers and containment facilities. Although no accurate data are available, estimates of total quantities reaching the world's oceans from these sources are 30 000-150 000 t·a^{-1} for total PAHs and 1-5 t·a^{-1} for benzo[a]pyrene (NRCC 1983). Elevated concentrations of PAHs have been recorded near specific point sources, such as creosoted material (Zitko 1975; Dunn and Fee 1979). No reliable information on the release of PAHs from land-based sources, such as municipal and industrial operations and surface runoff, is available. Estimates of 12 390 t·a^{-1} total PAHs and 978 t·a^{-1} benzo[a]pyrene discharged to the world's oceans from these sources have been reported. Surface runoff accounted for approximately 90-98% of these amounts (NRCC 1983).

6.3.14.1.3 Environmental Concentrations

PAHs are not uniformly distributed throughout the aquatic environment; instead, higher concentrations are generally encountered near point sources. PAH concentrations are expected to decrease approximately logarithmically with distance from the source. The majority of PAHs entering the aquatic environment are localized in rivers, lakes, estuaries and coastal marine waters. Concentrations of PAHs in aquatic ecosystems are generally highest in sediments, intermediate in aquatic biota and lowest in the water column (Neff 1979; NRCC 1983). Concentrations of PAHs are extremely variable, in part reflecting the degree of urban and industrial development and the specific use of the water (NRCC 1983). River water may contain significant concentrations of PAHs (0.02-3.79 µg·L^{-1} total PAHs) (Neff 1979); in general, there is a direct relationship between the concentration of PAHs in river water and the degree of industrialization and/or urbanization in the specific watershed (NRCC 1983). Groundwater usually contains PAHs at concentrations approximately one order of magnitude lower than those of surface waters (0.0009-4 µg·L^{-1} total PAHs) (Neff 1979), except in areas of specific localized contamination (NRCC 1983).

Because of their low water solubility and hydrophobic nature, PAHs tend to be associated primarily with inorganic and organic material in suspended and bed sediments (NRCC 1983). Concentrations of benzo[a]pyrene in freshwater sediments range from 0.001 to 17 µg·g^{-1} (dry weight) (Neff 1979). Several PAHs were identified in surficial and age-dated sediments from the Kitimat Arm downstream from an aluminum smelter in British Columbia (Cretney *et al.* 1982). PAH concentrations in sediments were found to be 10^3-10^4 times higher (up to 2829 µg·g^{-1} (dry weight) for 12 PAHs) than those found in the water column in Sydney Harbour, Nova Scotia (Environment Canada 1982).

Numerous reports have been published on the identification and quantification of PAHs, especially benzo[a]pyrene, in aquatic organisms; most of the available information concerns marine organisms. Benzo[a]pyrene concentrations range from nondetectable (usually <0.0001 µg·g^{-1} (dry weight)) to as high as 5 µg·g^{-1} (dry weight). Organisms collected near major industrial and domestic point sources usually have higher benzo[a]pyrene concentrations than do those organisms collected from more remote areas. However, from the available data, there is little apparent correlation between PAH concentrations in aquatic organisms and their phylatic position, trophic status and preferred habitat (Neff 1979). In general, filter-feeding bivalve molluscs have lower benzo[a]pyrene contents than do plankton and algae. Marine crustaceans usually contain low or undetectable concentrations of benzo[a]pyrene, as do most echinoderms. The benzo[a]pyrene content in fish is quite variable; demersal species do not appear to contain significantly higher amounts of benzo[a]pyrene than do pelagic species (Neff 1979).

Environmental concentration ranges for some PAHs in surface waters of the Atlantic region are presented in Table 6-152.

6.3.14.1.4 Forms and Fate in the Aquatic Environment

Polycyclic aromatic hydrocarbons are a diverse group of aromatic compounds containing two or more fused arene structures. In general, PAHs may be divided into two groups, depending upon their physical and chemical properties: low-molecular-weight PAHs, containing three or less aromatic rings, and high-molecular-weight PAHs, containing more than three aromatic rings. Although numerous aromatic configurations are possible, combined with a multitude of substitution patterns, most information on the forms and fate of PAHs in the aquatic environment is available for only a few compounds, specifically naphthalene, anthracene, benz[a]anthracene and benzo[a]pyrene (Figure 6-36).

PAHs are usually coloured, crystalline solids with high melting and boiling points, low vapour pressures and low water solubilities (Table 6-153) (Leo *et al.* 1971; U.S. EPA 1979; Neff 1979; Futoma *et al.* 1981; NRCC 1983). Although accurate data are lacking for many of these compounds, some general conclusions may be drawn from the available information. Low-molecular-weight PAHs are more soluble and volatile and have less affinity for surfaces than do high-molecular-weight PAHs. In general, vapour pressures decrease, as do water solubilities, with increasing molecular weight. PAHs with a linear arrangement of fused aromatic rings are usually less soluble than those having angular or pericondensed structures. Alkyl substitution usually decreases water solubility.

In general, most PAHs, with the exception of some low-molecular-weight compounds, will be strongly sorbed by particulate matter and biota in the aquatic environment. PAHs dissolved in the water column will be subject to photolysis. Volatilization of low-molecular-weight PAHs will also occur.

Table 6-152. Environmental Concentration Ranges for Some PAHs in Surface Waters of the Atlantic Region of Canada

PAH	Concentration range ($\mu g \cdot L^{-1}$)	Detection limit ($\mu g \cdot L^{-1}$)	Number of samples	Sampling year(s)
Benzo[a]pyrene	0.003	0.0002	61	1980-1981
Fluoranthene	0.005-0.01	0.0003	56	1980-1981
Benzo[b]-fluoranthene	<0.003	0.0005	61	1980-1981
Benzo[k]-fluoranthene	<0.002	0.0002	61	1980-1981
Benzo[g,h,i]-perylene	<0.006	0.0006	61	1980-1981
Indeno[1,2,3-cd]pyrene	<0.003-0.006	0.0015	58	1980-1981

Source: NAQUADAT 1985.

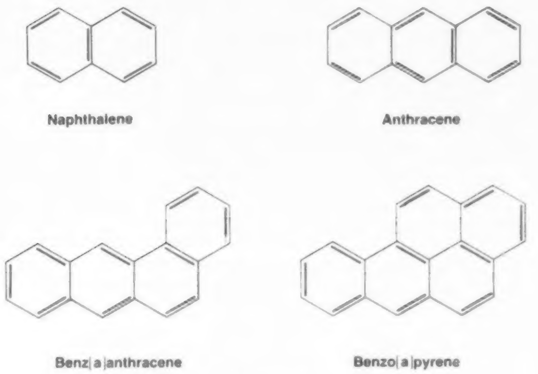


Figure 6-36. Examples of PAHs.

Those compounds accumulated in the sediments of aquatic systems will undergo some biodegradation and biotransformation (U.S. EPA 1980; NRCC 1983).

PAHs containing three or more rings have been shown to be sorbed rapidly and quantitatively by organic and inorganic material (Meyers and Quinn 1973; Herbes 1977). Sorption coefficients have been found to be high for several PAHs (10^4-10^6) (Smith *et al.* 1978). A high correlation between sediment sorption of PAHs and organic content has been demonstrated (Karickhoff *et al.* 1979; Means *et al.* 1982; Banwart *et al.* 1982). PAHs with less than three rings are not sorbed as extensively (Karickhoff *et al.* 1979). In field studies, sorption to suspended and bed sediments was found to be the primary removal mechanism for high-molecular-weight PAHs. On the other hand, volatilization and transport were the primary mechanisms operating for low-molecular-weight PAHs (Knap and Williams 1982; Readman *et al.* 1982). Although high-molecular-weight PAHs are associated primarily with particulate matter, a wide variety of soluble organic substances, including humic substances, may solubilize them and, hence, increase their aqueous mobility (Eganhouse and Calder 1976; Il'nitsky *et al.* 1979; Carlberg and Martinsen 1982).

The photooxidation of dissolved PAHs is relatively rapid under both laboratory and natural sunlight illumination; half-lives range from 30 min to 23 d. In natural waters, photolysis of dissolved PAHs proceeds at a slower rate; half-lives are 20-60% longer (Smith *et al.* 1978). Little or no photolysis occurs in the presence of particulate matter, because of either direct absorption or light scattering in the water column (McGinnes and Snoeyink 1974; Southworth 1979; Zepp and Schlotzhauer 1979; Oliver *et al.* 1979). However, benzo[a]pyrene is degraded rapidly in the presence of fulvic acid (half-life in pond water decreased from 173 to 43 h), probably because of increased solubilization or photosensitized reactions (Katz *et al.* 1979).

Low-molecular-weight PAHs, such as naphthalene compounds, are readily volatilized from the water column (NAS 1975). Although high-molecular-weight PAHs have low vapour pressures, they may also volatilize to a minor extent because of their poor aqueous solubility (Mackay *et al.* 1979). In general, volatilization half-lives from surfaces are longer than 100 h for high-molecular-weight PAHs, such as benz[a]anthracene and benzo[a]pyrene, and shorter than 100 h for low-molecular-weight PAHs, such as naphthalene and anthracene (Smith *et al.* 1978; Southworth 1979). However, these numbers may vary depending upon surface wind velocity and turbulence (Southworth 1979).

Neither chemical oxidation nor hydrolysis is expected to be a significant process in the removal of PAHs from natural water systems (Radding *et al.* 1976; Smith *et al.* 1978). Chlorination and ozonation of water have been found to reduce PAH concentrations (Harrison *et al.* 1976; Smith *et al.* 1978).

Some invertebrate and vertebrate species in the aquatic environment possess enzyme systems capable of metabolizing organic compounds such as PAHs (NRCC 1983). Few comprehensive studies of metabolism have been carried out with PAHs other than benzo[a]pyrene (Stegeman 1981). In general, mixed microbial populations in sediment-water systems may degrade some PAHs; the low-molecular-weight PAHs, such as naphthalene, are most easily degraded, with degradation progressively decreasing with increasing molecular weight. For PAHs with three or more rings, microbial degradation either does not occur or is very slow (Lee *et al.* 1978; Herbes 1981; Readman *et al.* 1982). Microbial degradation requires aerobic conditions (Delaune *et al.* 1981) and is enhanced in nutrient-rich laboratory systems (Fedorak and Westlake 1981). In addition, degradation may occur at a faster rate in oil-contaminated sediments than in pristine stream sediments (Herbes and Schwall 1978). Little or no enzymic

Table 6-153. Physical-chemical Properties of Some Polycyclic Aromatic Hydrocarbons

Compound	Molecular weight	Melting point (°C)	Vapour pressure (kPa (25°C))	Water solubility (mg·L^{-1} (25°C))	Octanol/water partition coefficient (log P_{ow})[1]
Fluorene	116.2	116-117	10^{-3}-10^{-4} [2]	1.69-1.98 [3]	4.18
Naphthalene	128.2	80.55	1.8×10^{-2} [4]	3.44 [3]	3.37
Acenaphthylene	152.2	92	10^{-3}-10^{-4} [2]	3.42 [3]	4.07
Acenaphthene	154.2	96	10^{-3}-10^{-4} [2]	3.42 [5]	4.33
Anthracene	178.2	218 (sublimes)	2.6×10^{-5}	0.03-0.08	4.45
Phenanthrene	178.2	100 (sublimes)	9.1×10^{-5}	1.0-1.8	4.46
Fluoranthene	202.2	110-111	10^{-5}-10^{-7} [2]	0.2-0.3	5.33
Pyrene	202.2	156	9.1×10^{-8}	0.1-0.2	5.32
Benz[a]anthracene	228.3	159-161	1.5×10^{-8}	$(9.4\text{-}11.4) \times 10^{-3}$	5.61
Chrysene	228.3	256	—	$(1.8\text{-}6) \times 10^{-3}$	5.61
Benzo[b]fluoranthene	252.3	167-168	—	—	6.57
Benzo[k]fluoranthene	252.3	216-217	1.3×10^{-11}	—	6.84
Benzo[a]pyrene	252.3	177-178	7.3×10^{-10}	$(0.2\text{-}6.1) \times 10^{-3}$	6.04
Benzo[e]pyrene	252.3	178-179	7.4×10^{-10}	—	—
Perylene	252.3	273-274	—	—	6.06
Benzo[ghi]perylene	276.3	277	1.3×10^{-11}	2.6×10^{-4} [3]	7.23
Indeno[1,2,3-cd]pyrene	276.3	163-164	10^{-11} [2]	—	7.66
Dibenzo[b,def]chrysene (Dibenzo[a,h]anthracene)	278.4	238	10^{-11} [2]	5.0×10^{-4}	5.97
Dibenzo[ghi,pqr]chrysene	300.4	438-440	2.0×10^{-13}	—	—
Coronene	302.4	272	—	—	—

[1] Leo *et al.* 1971; Radding *et al.* 1976.
[2] U.S. EPA 1979.
[3] Mackay and Shiu 1977.
[4] Cleland and Kingsbury 1977.
[5] Eganhouse and Calder 1976.

Sources: Leo *et al.* 1971; U.S. EPA 1979; Neff 1979; Futoma *et al.* 1981; NRCC 1983.

activity has been found in freshwater bivalves (Stegeman 1980; Payne *et al.* 1983), although some limited activity has been found in tissue preparations of a few species of crustaceans (Walters *et al.* 1979). Studies with fish species known to have high mixed-function oxidase activity show that they readily metabolize and depurate PAHs (Varanasi and Gmur 1981; NRCC 1983).

Evidence that some PAHs accumulate in the tissues of aquatic organisms at concentrations higher than those found in the surrounding water is available from field studies and studies using model ecosystems (NRCC 1983). Most studies have examined the parent PAHs, and little information is available on the accumulation of metabolic products. Although some PAHs have relatively high calculated octanol/water partition coefficients, measured bioaccumulation factors are lower than would be predicted. This may be the result of the difficulty in differentiating truly dissolved PAHs from "total" PAHs in the water. Bioconcentration factors of 10^2-10^3 were reported for *Daphnia pulex*, with factors increasing with molecular weight (Southworth *et al.* 1978). Bioconcentration factors of 10^2-10^4 were found for sediment and biota relative to water for benzo[a]pyrene (Il'nitsky *et al.* 1979). Oysters (*Crassostrea virginica*) had bioconcentration factors of 10^3 for PAHs with three rings (Lee *et al.* 1978).

In model ecosystems, high-molecular-weight PAHs were accumulated and magnified in lower organisms; however, fish were usually able to metabolize and depurate the compounds relatively rapidly, precluding biomagnification as a significant process (Lu *et al.* 1977). In general, although uptake of both low- and high-molecular-weight PAHs is relatively rapid in vertebrate species, metabolism and depuration are also rapid. For example, biological half-lives of approximately 6-9 d were found for two- and three-ringed PAHs in rainbow trout (*Salmo gairdneri*). Estimates of whole-body half-lives for a variety of PAHs were usually less than 7 d in a number of different fish species (Niimi and Palazzo 1985). Hence, bioaccumulation of PAHs, at least for vertebrate species, is considered to be relatively short-term in the aquatic environment (U.S. EPA 1979; NRCC 1983).

6.3.14.1.5 References

Banwart, W.L., J.J. Hassett, S.G. Wood and J.C. Means. 1982. Aquatic distribution of heterocyclic compounds by soils and sediments. Soil Sci. 133: 42-47.

Carlberg, G.E. and K. Martinsen. 1982. Adsorption/complexation of organic micropollutants to aquatic humus. Influence of aquatic humus with time on organic pollutants and comparison of two analytical methods for analyzing organic pollutants in humus water. Sci. Total Environ. 25: 245-254.

Cleland, J.G. and G.L. Kingsbury. 1977. Multimedia Environmental Goals for Environmental Assessment. Vol. II. MEG Charts and Background Information. U.S. Environmental Protection Agency, Washington, D.C. 451 pp.

Cretney, W.J., C.S. Wong, R.W. Macdonald, P.E. Erickson and B.R. Fowler. 1982. Polycyclic aromatic hydrocarbons in surface sediments and age-dated cores from Kitimat Arm, Douglas Channel and adjoining waterways. Can. Tech. Rep. Hydrogr. Ocean Sci. 18: 162-165.

Delaune, R.D., W.H. Patrick and M.E. Casselman. 1981. Effect of sediment pH and redox conditions in degradation of benzo[a]pyrene. Mar. Pollut. Bull. 12: 251-253.

Dunn, B.P. and J. Fee. 1979. Polycyclic aromatic hydrocarbon carcinogens in commercial seafood. J. Fish. Res. Board Can. 36: 1469-1476.

Eganhouse, R.P. and J.A. Calder. 1976. The solubility of medium weight aromatic hydrocarbons and the effect of hydrocarbon co-solutes and salinity. Geochim. Cosmochim. Acta 40: 555-561.

Eisenreich, S.J., B.B. Looney and J.B. Thornton. 1981. Airborne organic contaminants in the Great Lakes ecosystem. Environ. Sci. Technol. 15: 30-38.

Environment Canada. 1982. Investigation of Polycyclic Aromatic Hydrocarbon Contamination of Sydney Harbour, Nova Scotia (an Interim Report). Environmental Protection Service, Environment Canada. 34 pp.

Fedorak, P.M. and D.W.S. Westlake. 1981. Microbial degradation of aromatics and saturates in Prudhoe Bay crude oil as determined by glass capillary gas chromatography. Can. J. Microbiol. 27: 432-443.

Futoma, D.J., S.R. Smith, T.E. Smith and J. Tanaka. 1981. Polycyclic Aromatic Hydrocarbons in Water Systems. CRC Press Inc., Boca Raton, Florida. p. 190.

Gschwend, P.M. and R.A. Hites. 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim. Cosmochim. Acta 45: 2359-2367.

Harrison, R.M., R. Perry and R.A. Wellings. 1976. Chemical kinetics of chlorination of some polynuclear aromatic hydrocarbons under conditions of water treatment processes. Environ. Sci. Technol. 10: 1156-1160.

Herbes, S.E. 1977. Partitioning of polycyclic aromatic hydrocarbons between dissolved and particulate phase in natural waters. Water Res. 11: 493-496.

Herbes, S.E. 1981. Rates of microbial transformation of polycyclic aromatic hydrocarbons in water and sediments in the vicinity of a coal-coking wastewater discharge. Appl. Environ. Microbiol. 41: 20-28.

Herbes, S.E. and L.R. Schwall. 1978. Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments. Appl. Environ. Microbiol. 35: 306-316.

Hites, R.A. and P.M. Gschwend. 1982. The ultimate fates of polycyclic aromatic hydrocarbons in marine and lacustrine sediments. *In* Proc. 6th Int. Symp. on Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry. M. Cooke, A.J. Dennis and G.L. Fisher (eds.). Battelle Press, Columbus, Ohio. pp. 357-366.

Il'nitsky, A.P., J.L. Lembik, L.G. Solenova and L.M. Shabad. 1979. On the distribution of benzo[a]pyrene among different objects of the aqueous medium in water bodies. Cancer Det. Prev. 2: 471-483.

Karickhoff, S.W., D.J. Brown and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13: 241-248.

Katz, M., C. Chan, H. Tosine and T. Sakuma. 1979. Relative rates of photochemical and biological oxidation (*in vitro*) of polynuclear aromatic hydrocarbons. *In* Polynuclear Aromatic Hydrocarbons. 3rd Int. Symp. on Chemistry and Biology – Carcinogenesis and Mutagenesis. P.W. Jones and P. Leber (eds.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 171-189.

Knap, A.H. and P.J. Le B. Williams. 1982. Experimental studies to determine the fate of petroleum hydrocarbons from refinery effluent in an estuarine system. Environ. Sci. Technol. 16: 1-4.

Lee, R.F., W.S. Gardner, J.W. Anderson, J.W. Blaylock and J. Barwell-Clark. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 12: 832-838.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71: 525-616.

Lu, A.Y.H., R.L. Metcalf, N. Plummer and D. Mandel. 1977. The environmental fate of three carcinogens: Benzo[a]pyrene, benzidine and vinyl chloride evaluated in laboratory model ecosystems. Arch. Environ. Contam. Toxicol. 6: 129-142.

Mackay, D. and W.Y. Shiu. 1977. Aqueous solubility of polynuclear aromatic hydrocarbons. Chem. Eng. Data 22: 399-402.

Mackay, D., W.Y. Shiu and R.P. Sutherland. 1979. Determination of air-water Henry's law constants for hydrophobic pollutants. Environ. Sci. Technol. 13: 333-337.

McGinnes, P.R. and V.L. Snoeyink. 1974. Determination of the fate of polynuclear aromatic hydrocarbons in natural water systems. Univ. of Illinois, Urbana-Champaign, Water Resources Center Res. Rep. No. 80. 56 pp. (Cited in NRCC 1983.)

Means, J.C., S.G. Wood, J.J. Hassett and W.L. Banwart. 1982. Sorption of amino- and carboxy- substituted polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol. 16: 93-97.

Meyers, P.A. and J.G. Quinn. 1973. Association of hydrocarbons and mineral particles in saline solutions. Nature (London) 244: 23-24.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

NAS. 1975. Petroleum in the Marine Environment. Workshop on Inputs, Fates and Effects of Petroleum in the Marine Environment, Airlie, Virginia, May 21-25, 1973. U.S. National Research Council, National Academy of Sciences, Washington, D.C. 107 pp.

Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Sources, Fate and Biological Effects. Applied Science Publ. Ltd., London. 262 pp.

Niimi, A.J. and V. Palazzo. 1986. Biological half-lives of eight polycyclic aromatic hydrocarbons (PAHs) in rainbow trout (*Salmo gairdneri*). Water Res. (in press).

NRCC. 1983. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects on Aquatic Biota. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18981. 209 pp.

Oliver, B.A., E.G. Cosgrove and J.H. Carey. 1979. Effect of suspended sediments in the photolysis of organics in water. Environ. Sci. Technol. 13: 1075-1077.

Payne, J.F., A. Rahimtula and S. Lim. 1983. Metabolism of petroleum hydrocarbons by marine organisms: The potential of bivalve molluscs. *In* Proc. Can. Fed. Biol. Soc. 26th Annual Meeting, June 13-17, Ottawa.

Radding, S.B., T. Mill, C.W. Gould, D.H. Liu, H.L. Johnson, D.C. Bomberger and C.V. Fojo. 1976. The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/5-755-009. 122 pp.

Readman, J.W., R.F.C. Mantoura, M.M. Rhead and L. Brown. 1982. Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary. Estuarine Coastal Shelf Sci. 14: 369-389.

Seuss, M.J. 1976. The environmental load and cycle of polycyclic aromatic hydrocarbons. Sci. Total Environ. 6: 239-250.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.-W. Chou, D.C. Bomberger and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems. II. Laboratory Studies. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/7-78-074

Southworth, G.R. 1979. Transport and transformation of anthracene in natural waters. *In* Proc. 2nd Annu. Symp. on Aquatic Toxicology. ASTM STP 667. L.L. Marking and R.A. Kimerle (eds.). Am. Soc. Test. Mater., Cleveland, Ohio. pp. 507-514.

Southworth, G.R., J.J. Beauchamp and P.K. Schmieder. 1978. Bioaccumulation potential of polycyclic aromatic hydrocarbons in *Daphnia pulex*. Water Res. 12: 973-977.

Stegeman, J.J. 1980. Mixed-function oxygenase studies in monitoring for effects of organic pollution. Rapp. P.V. Reun. Cons. Int. Explor. Mer 179: 33-38.

Stegeman, J.J. 1981. Polynuclear aromatic hydrocarbons and their metabolism in the marine environment. *In* Polycyclic Aromatic Hydrocarbons and Cancer. Vol. 3. H.V. Gelboin and P.O.P. Ts'o (eds.). Academic Press, New York. pp. 1-59.

U.S. EPA. 1979. Polycyclic aromatic hydrocarbons. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. II. Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. pp. 95-1 to 97-23.

U.S. EPA. 1980. Ambient Water Quality Criteria for Polynuclear Aromatic Hydrocarbons (PAHs). Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-069.

Varanasi, U. and D.J. Gmur. 1981. *In vivo* metabolism of naphthalene and benzo[a]pyrene by flatfish. *In* Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons. 5th Int. Symp. M. Cooke and A.J. Dennis (eds.). Batelle Press, Columbus, Ohio. pp. 367-376.

Wakeham, S.G., C. Schaffner and W. Giger. 1980. Polycyclic aromatic hydrocarbons in recent lake sediments. II. Compounds derived from biogenic precursors during early diagenesis. Geochim. Cosmochim. Acta 44: 414-429.

Walters, J.M., R.B. Cain, I.J. Higgins and E.D.S. Corner. 1979. Cell-free benzo[a]pyrene hydroxylase activity in marine zooplankton. J. Mar. Biol. Assoc. U.K. 59: 553-563.

Zepp, R.G. and P.F. Schlotzhauer. 1979. Photoreactivity of selected aromatic hydrocarbons in water. *In* Polynuclear Aromatic Hydrocarbons. 3rd Int. Symp. on Chemistry and Biology – Carcinogenesis and Mutagenesis. P.W. Jones and P. Leber (eds.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 141-158.

Zitko, V. 1975. Aromatic hydrocarbons in aquatic fauna. Bull. Environ. Contam. Toxicol. 14: 621-631.

6.3.14.2 Polybrominated Biphenyls (PBBs)

6.3.14.2.1 Uses and Production

Polybrominated biphenyls (PBBs) are a complex mixture of compounds (more than 42) that have a bromine-substituted biphenyl nucleus in common. They have been used almost exclusively as fire retardants in plastics and synthetic fibres employed in the communications and electrical industries (Jamieson 1977).

PBBs have been manufactured only in the U.S.A. and Germany. U.S. production totalled 5×10^6 kg between 1970 and 1974, and was confined to only two plants. The Michigan Chemical Corporation plant in St. Louis, Michigan, produced 99% of the U.S. total. Use of PBBs in the U.S.A. in 1974 amounted to approximately 1.2×10^6 kg. No PBBs appear to have been produced between 1975 and 1978 (Jamieson 1977).

In Canada, 0.6×10^6 kg PBBs were used as a fire-retardant additive between 1972 and 1975 (Jamieson 1977). Polybrominated biphenyls have been prohibited from use in all commercial manufacturing and processing since May 1, 1979, in Canada (Environment Canada 1985).

Additional names for PBBs sold in Canada include Firemaster BP-6; Technical Octabromobiphenyl; and Technical Decabromobiphenyl (Environment Canada 1985). Polybrominated biphenyls were included in the importation into Canada of formulated fire retardants (plastic compounding) between 1981 and 1983. The amounts imported were 126.3 t (1981); 147.5 t (1982); and 153.2 t (1983) (Statistics Canada 1983, 1984).

6.3.14.2.2 Sources and Pathways for Entering the Aquatic Environment

Because of the immobile nature of the finished product, large amounts of PBBs are not expected to enter the environment. The identifiable pathways by which PBBs would be expected to enter the environment are manufacturing plant effluents, accidental introductions and product use and disposal (Jamieson 1977).

6.3.14.2.3 Environmental Concentrations

The only reports of the presence of PBBs in the aquatic environment are related to production and industrial use. The Pine River, which is part of the Saginaw River system flowing into Saginaw Bay, Lake Huron, receives effluent from the Michigan Chemical Corporation plant, where concentrations as high as 3.2 $\mu g \cdot L^{-1}$ in water were reported. Concentrations decreased downstream, falling to 0.01 $\mu g \cdot L^{-1}$ at a point 13 km from the plant. PBB concentrations in sediment in the same area decreased from 77 000 to 100 $\mu g \cdot kg^{-1}$ about 38 km downstream (Hesse 1974, 1975a, b). A later survey showed no detectable PBB concentrations in water, and a maximum of 1200 $\mu g \cdot kg^{-1}$ in sediment (Powers 1976).

Concentrations of PBBs in raw and treated wastewater from an industrial plant in Cobourg, Ontario, were 0.7 and 0.01 $\mu g \cdot L^{-1}$, respectively (Abbott 1975). PBBs were not detected (detection limit 0.08 $\mu g \cdot L^{-1}$) in water samples taken downstream from a dump site for sludges from the plant (Abbott 1976).

Measurements of PBBs in biota have been reported, but only in areas in the U.S.A. near industrial production and use. In the Pine River in Michigan, measurable concentrations (0.09 $mg \cdot kg^{-1}$) have been detected as far as 13 km downstream from the plant, with highest concentrations (1.33 $mg \cdot kg^{-1}$ carp fillet, wet weight) near the plant (Hesse 1974, 1975a, b). Low but measurable concentrations in birds and mammals near the Michigan site have been reported (Tanner 1977). No PBBs were found in aquatic biota near the Canadian industrial site (Abbott 1976).

6.3.14.2.4 Forms and Fate in the Aquatic Environment

Polybrominated biphenyls are halogen-substituted biphenyl compounds containing between one and eight bromine atoms. The compounds are either solids or liquids at room temperature; in general, melting points and boiling points increase with increasing bromine substitution (Sundström *et al.* 1976). Vapour pressures of PBBs appear to be low (<1 Pa at 20°C) (Jamieson 1977). Although PBBs have a demonstrated affinity for organic matter, very little information is available on their fate in the aquatic environment (Jamieson 1977).

PBBs contained in commercial formulations have been found to be persistent in soils, with only one pentabromobiphenyl compound showing any significant disappearance after 24 weeks of incubation (Jacobs *et al.* 1976). 2,2′,4,4′,5,5′-Hexabromobiphenyl was readily sorbed by the soils in Michigan, with sorption increasing proportionally with organic carbon content. Desorption was reported to be relatively low (Filonow *et al.* 1976).

No information is available on the photolysis of PBBs in aqueous systems; however, they appear to be rapidly photochemically degraded in nonaqueous solvents. For example, less than 10% of 2,2′,4,4′,5,5′-hexabromobiphenyl remained in methanol solution after ultraviolet irradiation for 10 min (Anderson *et al.* 1974). Commercial formulations were also rapidly photodegraded in methanol (Ruzo and Zabik 1975).

Although the potential for bioaccumulation exists (e.g. calculated log octanol/water partition coefficient for octabromobiphenyl is 5.53) (Jamieson 1977), few reliable studies have been performed. Caged fathead minnows (*Pimephales promelas*) held near the outfalls and 1.6 km downstream of the Michigan Chemical Corporation plant in St. Louis, Michigan, accumulated PBBs to 1000-10 000 times the concentration found in the water (Hesse 1974). In addition, PBBs have been detected in wild ducks in Michigan (Powers 1976), in herring gulls and eggs in the Great Lakes and in terrestrial birds and mammals (Tanner 1977). No evidence of PBB contamination was found in Coho salmon (*Oncorhynchus kisutch*) taken from Lake Ontario (Abbott 1976). In a laboratory study using static conditions and nominal concentrations, juvenile Atlantic salmon (*Salmo salar*) exposed to PBBs for up to 96 h accumulated detectable quantities of a pentabromobiphenyl and 2,2′,4,4′,5,5′-hexabromobiphenyl. A heptabromobiphenyl was not detected. When administered in food, higher concentrations of PBBs were detected in fish. The accumulation of PBBs appeared to decrease with increasing bromine substitution; however, because of the low water solubility of the PBBs, the exposure was probably not of sufficient duration to attain equilibrium. Several lower brominated compounds were detected, suggesting that some metabolism by either the fish or associated microflora took place (Zitko 1977).

6.3.14.2.5 References

Abbott, R.A. 1975. Summary report on the usage and loss of polybrominated biphenyls from plastics manufacturing in Ontario. Petroleum and Chemical Unit, Industrial Section, Pollution Control Branch, Ontario Ministry of the Environment. (Cited in Jamieson 1977.)

Abbott, R.A. 1976. Personal communication. Environment Canada. (Cited in Jamieson 1977.)

Anderson, K., A. Norstrom, C. Rappe, B. Rasmuson and H. Swahlin. 1974. Photochemical degradation of PCB, PBB and other flame retardants. *In* Proc. 34th Int. Conf. on Pesticides, Helsinki, Finland. pp. 798-802. (Cited in Jamieson 1977.)

Environment Canada. 1985. Polybrominated biphenyls. *In* Canada Gazette Announcements – Environmental Contaminants Act. Environmental Protection Service, Ottawa. pp. 1 and 51.

Filonow, A.B., L.W. Jacobs and M.M. Mortland. 1976. Fate of polybrominated biphenyls (PBBs) in soils. Retention of hexabromobiphenyl in four Michigan soils. J. Agric. Food Chem. 24: 1201-1204.

Hesse, J.L. 1974. Water Pollution Aspects of Polybrominated Biphenyl Production: Results of Initial Surveys in the Pine River in the Vicinity of St. Louis, Michigan. Presentation to Governor's Great Lakes Regional Interdisciplinary Pesticide Council, Oct. 17, 1974. Water Quality Appraisal Section, Bureau of Water Management, Michigan Department of Natural Resources, Lansing, Michigan. (Cited in Jamieson 1977.)

Hesse, J.L. 1975a. Water Pollution Aspects of Polybrominated Biphenyl Production: Results of Surveys in the Pine River in the Vicinity of St. Louis, Michigan. Presented at the 2nd Natl. Conf. on Complete Water Reuse, Chicago, Illinois, May 4-8, 1975. Bureau of Water Management, Michigan Department of Natural Resources, Lansing, Michigan. (Cited in Jamieson 1977.)

Hesse, J.L. 1975b. Discussion following presentation of paper by H.E.B. Humphrey, and N.S. Hayner. Proc. Univ. Mo. Annu. Conf. Trace Subst. Environ. Health 9: 57-63. (Cited in Jamieson 1977.)

Jacobs, L.W., S.-F. Chou and J.M. Tiedje. 1976. Fate of polybrominated biphenyls (PBBs) in soils. Persistence and plant uptake. J. Agric. Food Chem. 24: 1198-1201.

Jamieson, J.W.S. 1977. Polybrominated Biphenyls in the Environment. Environmental Impact Control Directorate, Fisheries and Environment Canada. Economic and Technical Review Report EPS-3-EC-77-18. 71 pp.

Powers, R.A. 1976. Status of polybrominated biphenyl (PBB) contamination of the Pine River, Gratiot and Midland Counties, Michigan. Toxic Materials Section, Water Quality Division, Environmental Protection Bureau, Michigan Department of Natural Resources, Lansing, Michigan. (Cited in Jamieson 1977.)

Ruzo, L.O. and M.J. Zabik. 1975. Polyhalogenated biphenyls: photolysis of hexabromo and hexachlorobiphenyls in methanol solution. Bull. Environ. Contam. Toxicol. 13: 181-182.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Statistics Canada. 1984. Imports: Merchandise Trade, Commodity Detail 1983. Catalogue No. 65-207.

Sundström, G., O. Hutzinger, S. Safe and V. Zitko. 1976. The synthesis and gas chromatographic properties of bromobiphenyls. Sci. Total Environ. 6: 15-29.

Tanner, H.A. 1977. Testimony on polybrominated biphenyls. Senate Commerce Committee Hearings, Michigan Department of Natural Resources, March 30. (Cited in Jamieson 1977.)

Zitko, V. 1977. The accumulation of polybrominated biphenyls by fish. Bull. Environ. Contam. Toxicol. 17: 285-292.

6.3.14.3 Polychlorinated Dibenzo-*p*-Dioxins (PCDDs)

6.3.14.3.1 Uses and Production

Polychlorinated dibenzo-*p*-dioxins (PCDDs) have no use as such, and result from various synthetic or pyrolytic reactions. PCDDs are known to exist in a variety of chemicals used, or formerly used, as pesticides, especially the herbicides 2,4,5-T, Silvex and 2,4-D. The wood preservative, pentachlorophenol (PCP), and chlorinated phenols, such as trichlorophenol and tetrachlorophenol, can also contain PCDDs. Combustion processes, including the burning of fossil fuels, wood and garbage, can lead to the formation of PCDDs. PCDDs have been found in the fly ash of combustion facilities, such as municipal and industrial incinerators (NRCC 1981).

6.3.14.3.2 Sources and Pathways for Entering the Aquatic Environment

The major pathways for the entry of PCDDs into the environment include the use of PCDD-contaminated chemicals, such as chlorinated phenols used in the treatment of wood; the broadcast application of pesticides containing PCDD as a contaminant; the disposal of chemicals contaminated with PCDDs; and stack emissions and exhaust from combustion facilities, including municipal incinerators. Forest fires also represent a potential source of PCDDs (NRCC 1981).

The annual input of PCDDs to the Canadian environment is estimated at 1.5 t, although this is qualified on the basis of inexact data and uncertainty as to the isomeric makeup of the PCDDs emitted (NRCC 1981).

6.3.14.3.3 Environmental Concentrations

Until recently, no published data were available on levels of PCDDs in Canadian waters. A report by Environment Canada/Ontario Ministry of the Environment (1981) showed that 2,3,7,8-TCDD was not detectable in 75 samples of Great Lakes water. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) was not detected (detection limit 10 $ng \cdot L^{-1}$) in any of the 41 samples taken from the surface waters of the lower and upper Niagara River in 1979 and 1980. Similarly, no detectable levels (detection limit 10 $ng \cdot L^{-1}$) were observed in 25 samples of treated drinking water taken from three cities on the upper Niagara River in 1980 (Environment Canada/Ontario Ministry of the Environment 1981). U.S. reports are similar in their lack of detectable residues. This has been partly attributed to the low water solubility of these compounds, but is also the result of the absence, until quite recently, of a systematic monitoring program for these compounds, which are likely to occur only at very low levels.

There is also little information on residue levels in aquatic invertebrates. According to one source (Jones 1981), only one published reference exists concerning PCDD levels in North American invertebrates, and this study (Young *et al.* 1975) did not detect any PCDD. In areas of South Vietnam heavily exposed to 2,4,5-T, prawns (crustaceans) were shown to contain residues of 2,3,7,8-TCDD at concentrations ranging from 18 to 42 ng·kg^{-1} (Baughman and Meselson 1973).

Reports of PCDDs in Lake Ontario fish were initially based on the detection of an unidentified dioxin in two fish taken on the American side in 1979. In a subsequent news release (August, 1981) by the New York State Health Department, dioxins were reported in 50 fish from Lake Ontario, at residue concentrations up to 162 ng·kg^{-1} and averaging 24.3 ng·kg^{-1} 2,3,7,8-TCDD. By contrast, Great Lakes fish collected by the Ontario Ministry of the Environment showed only trace levels in a few cases (detection limit 10 ng·kg^{-1}). Fish samples (six yellow perch and one smallmouth bass) taken in the upper Niagara River in 1980 did not contain any detectable concentrations of 2,3,7,8-TCDD at the 10 ng·kg^{-1} detection limit. In Lake Ontario, TCDD was detected in fillets of 23 of 61 sports fish from various locations (chiefly western Lake Ontario) at a concentration range of nondetectable (10 ng·kg^{-1}) to 20 ng·kg^{-1} (Environment Canada/Ontario Ministry of the Environment 1981).

A study of herring gull eggs collected throughout the Great Lakes Basin in 1979 detected 2,3,7,8-TCDD at trace concentrations (>1 ng·kg^{-1}) in all eggs sampled and at elevated levels in Saginaw Bay, Lake Michigan and Lake Ontario. Waste disposal or major accidents during the manufacturing of 2,4,5-trichlorophenol are the most likely sources of the higher levels of TCDD found in Lake Ontario and the Niagara River (Environment Canada/Ontario Ministry of the Environment 1981).

6.3.14.3.4 Forms and Fate in the Aquatic Environment

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are a group of chemicals composed of 75 chemically related compounds or congeners having the basic aromatic nucleus shown in Figure 6-37.

PCDD congeners range in degree of chlorine substitution from one to eight; there are 2 mono-, 10 di-, 14 tri-, 22 tetra-, 14 penta-, 10 hexa- and 1 octachlorinated compounds. Although a very diverse group, PCDDs do have a number of common properties, including a relatively stable aromatic nucleus. The more highly chlorinated congeners have a relative inertness towards acids, bases, oxidation, reduction and heat. In addition, increased chemical and environmental stability and lipophilicity occur with increasing chlorine substitution (NRCC 1981).

In general, very little information is available on the forms and fate of PCDDs in the aquatic environment, and, hence, the major removal processes have not been quantitatively elucidated (U.S. EPA 1979; NRCC 1981). Most of the available information on PCDDs pertains to only one congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). TCDD has a molecular weight of 322, a melting point of 303-305°C and a water solubility of 0.2 µg·L^{-1} (Crummett and Stehl 1973). However, many of the studies examining the environmental dynamics of TCDD are qualitative in nature and, thus, do not provide adequate data for the quantification of removal processes (U.S. EPA 1979; NRCC 1981).

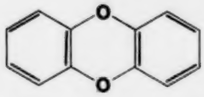


Figure 6-37. Basic aromatic nucleus of PCDDs.

PCDDs tend to be rapidly and strongly sorbed to most soils and sediments, with the degree of sorption being related to organic content (Isensee and Jones 1975; Ward and Matsumura 1976, 1977, 1978; Firestone 1977). An octanol/water partition coefficient (P_{ow}) of 1.4×10^6 and an organic carbon partition coefficient (K_{oc}) of 4.7×10^5 have been reported (Kenaga 1980). Quantitative information, however, on the rate, extent and environmental significance of sorption is lacking (U.S. EPA 1979; NRCC 1981).

PCDDs may undergo photolysis when deposited onto foliar surfaces and, to a lesser extent, in soils. The presence of hydrogen donors, such as alcohols, ethers, hydrocarbons and natural products, such as waxes, and ultraviolet light of appropriate wavelength are required (Choudhry and Hutzinger 1982; Young 1983). Little quantitative information is, however, available regarding the rate and extent of photolysis in natural systems. The primary photolytic degradation pathway involves dechlorination to less chlorinated congeners. In pure water, very little photolysis occurs (Crosby *et al.* 1971; Plimmer *et al.* 1973; Ward and Matsumura 1977; Plimmer 1978; Parlar *et al.* 1978; Liberti *et al.* 1978; Dobbs and Grant 1979). The higher chlorinated congeners, such as octachlorodibenzo-*p*-dioxin, are less reactive than the lower chlorinated congeners, such as the trichlorinated dioxins (NRCC 1981).

Quantitative data on volatilization from surface waters are limited. The predicted volatilization half-life of 2,3,7,8-TCDD in water of 1-cm depth was 2 d; in water of 1-m depth, the half-life increased to 200 d (NRCC 1981). In contrast, the volatilization half-life of 2,3,7,8-TCDD was estimated to be 5.5 and 12 years in a pond and a lake, respectively (U.S. EPA 1983).

Experimental studies have indicated that PCDDs are highly resistant to microbial degradation (Kearney *et al.* 1972; Matsumura and Benezet 1973; Ward and Matsumura 1976; Klecka and Gibson 1980). Half-lives in biologically active soils and sediments range from 1-2 years (Helling *et al.* 1973; Young *et al.* 1976; Ward and Matsumura 1976) to as much as 10 years (DiDomenico *et al.* 1980) or more (Kimbrough *et al.* 1983). In aquatic microcosms, TCDD was not degraded under aerobic conditions (Isensee and Jones 1975).

TCDD is readily bioaccumulated by a number of aquatic organisms. Using a model aquatic ecosystem, bioconcentration factors for a variety of aquatic organisms were between 2000 and 6000 (Yochim *et al.* 1978). Bioconcentration factors of up to 10^4 have been reported (Isensee and Jones 1975; Isensee 1978). Fish apparently do not accumulate TCDD via dietary exposure (Hawkes and Norris 1977).

6.3.14.3.5 References

Baughman, R. and M. Meselson. 1973. An analytical method for detecting TCDD (Dioxin): Levels of TCDD in samples from Vietnam. Environ. Health Perspect. 5: 27-35. (Cited in Jones 1981.)

Choudhry, G.G. and O. Hutzinger. 1982. Photochemical formation and degradation of polychlorinated dibenzo-furans and dibenzo-*p*-dioxins. Residue Rev. 84: 113-161.

Crosby, D.G., A.S. Wong, J.R. Plimmer and E.A. Woolson. 1971. Photodecomposition of chlorinated dibenzo-*p*-dioxins. Science 173: 748-749. (Cited in U.S. EPA 1979.)

Crummett, W.B. and R.H. Stehl. 1973. Determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans in various materials. Environ. Health Perspect. 5: 15-25.

DiDomenico, A., V. Silano, G. Viviano and G. Zapponi. 1980. Accidental release of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) at Seveso, Italy. V. Environmental persistence of TCDD in soil. Ecotoxicol. Environ. Saf. 4: 339-345. (Cited in NRCC 1981.)

Dobbs, A.J. and C. Grant. 1979. Photolysis of highly chlorinated dibenzo-*p*-dioxins by sunlight. Nature (London) 278: 163-165. (Cited in NRCC 1981.)

Environment Canada/Ontario Ministry of the Environment. 1981. Environmental Baseline Report of the Niagara River. Canada-Ontario Agreement on Great Lakes Water Quality, Canada-Ontario Review Board, Ottawa.

Firestone, D. 1977. Chemistry and analysis of pentachlorophenol and its contaminants. FDA By-lines 2: 57-89. (Cited in NRCC 1981.)

Hawkes, C.L. and L.A. Norris. 1977. Chronic oral toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to rainbow trout. Trans. Am. Fish. Soc. 106: 641-645. (Cited in NRCC 1981.)

Helling, C.S., A.R. Isensee, E.A. Woolson, P.D.J. Ensor, G.E. Jones, J.R. Plimmer and P.C. Kearney. 1973. Chlorodioxins in pesticides, soils, and plants. J. Environ. Qual. 2: 171-178. (Cited in U.S. EPA 1979.)

Isensee, A.R. 1978. Bioaccumulation of 2,3,7,8-tetrachlorodibenzo-para-dioxin. Ecol. Bull. 27: 255-262. (Cited in NRCC 1981.)

Isensee, A.R. and G.E. Jones. 1975. Distribution of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (TCDD) in an aquatic model ecosystem. Environ. Sci. Technol. 9: 668-672. (Cited in U.S. EPA 1979.)

Jones, P.A. 1981. Chlorophenols and their Impurities in the Canadian Environment. Environmental Protection Service, Environment Canada, Ottawa. Economic and Technical Report EPS 3-EC-81-2. 435 pp.

Kearney, P.C., E.A. Woolson and C.P. Ellington, Jr. 1972. Persistence and metabolism of chlorodioxins in soils. Environ. Sci. Technol. 6: 1017-1019. (Cited in U.S. EPA 1979.)

Kenaga, E.E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. Environ. Sci. Technol. 14: 553-556. (Cited in NRCC 1981.)

Kimbrough, R.D., H. Falk, P. Stehr and G. Fries. 1983. Health implications of 2,3,7,8-tetrachlorodibenzo dioxin (TCDD) contamination of residential soil. J. Toxicol. Environ. Health 14: 47-93.

Klecka, G.M. and D.T. Gibson. 1980. Metabolism of dibenzo-*p*-dioxin and chlorinated dibenzo-*para*-dioxins by a *Beijerinckia* species. Appl. Environ. Microbiol. 39: 288-296. (Cited in NRCC 1981.)

Liberti, A., D. Brocco, I. Allegrini, A. Cecinato and M. Possanzini. 1978. Solar and UV photodecomposition of 2,3,7,8-tetrachlorodibenzo-*para*-dioxin in the environment. Sci. Total Environ. 10: 97-104. (Cited in U.S. EPA 1979.)

Matsumura, F. and H.J. Benezet. 1973. Studies on the bioaccumulation and microbial degradation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Environ. Health Perspect. 5: 253-258. (Cited in U.S. EPA 1979.)

NRCC. 1981. Polychlorinated Dibenzo-*p*-dioxins. Criteria for their Effects on Man and his Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18574. 251 pp.

Parlar, H., S. Gaeb and I. Gebefügi. 1978. Photochemical reactions of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) adsorbed on a silica gel. Pergamon Ser. Environ. Sci. 1: 465-466. (Cited in NRCC 1981.)

Plimmer, J.R. 1978. Photolysis of TCDD and trifluralin on silica and soil. Bull. Environ. Contam. Toxicol. 20: 87-92. (Cited in NRCC 1981.)

Plimmer, J.R., U.I. Klingebiel, D.C. Crosby and A.S. Wong. 1973. Photochemistry of dibenzo-*p*-dioxins. *In* Chlorodioxins – Origin and Fate. E.H. Blair (ed.). Adv. Chem. Ser. No. 120. pp. 44-54. (Cited in NRCC 1981.)

U.S. EPA. 1979. TCDD. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, and Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 34-1 to 34-9.

U.S. EPA. 1983. Dioxin Strategy. U.S. Environmental Protection Agency, Washington, D.C. 43 pp.

Ward, C.T. and F. Matsumura. 1976. Studies on the Degradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) in Lake Water and Sediments. Office of Water Research and Technology, Washington, D.C. U.S. Dep. Commerce. NTIS Rep. PB-264881. (Cited in NRCC 1981.)

Ward, C.T. and F. Matsumura. 1977. Fate of 2,4,5-T Contaminant, 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) in Aquatic Environments. Office of Water Research and Technology, Washington, D.C. U.S. Dep. Commerce. NTIS Rep. PB-264187. (Cited in U.S. EPA 1979.)

Ward, C.T. and F. Matsumura. 1978. Fate of 2,3,7,8-tetrachlorodibenzo- *p*-dioxin (TCDD) in a model aquatic environment. Arch. Environ. Contam. Toxicol. 7: 349-357. (Cited in NRCC 1981.)

Yochim, R.S., A.R. Isensee and G.E. Jones. 1978. Distribution and toxicity of TCDD and 2,4,5-T in an aquatic model ecosystem. Chemosphere 7: 215-220.

Young, A.L. 1983. Long-term studies on the persistence and movement of TCDD in a natural ecosystem. *In* Human and Environmental Risks of Chlorinated Dioxins and Related Compounds. R.E. Tucker, A.L. Young and A.P. Gray (eds.). Plenum Press, New York. pp. 173-190.

Young, A.L., C.E. Thalken and W.E. Ward. 1975. Studies on the Ecological Impact of Repetitive Aerial Application of Herbicides on the Ecosystem of Test Area C-52A, Eglin AFB, Florida. U.S. Air Force Armament Lab., Eglin Air Force Base, Florida. Tech. Rep. No. AFATL-TR-75-142. (Cited in Jones 1981.)

Young, A.L., J.A. Calcagni, C.E. Thalkeu and J.W. Tremblay. 1976. The toxicology, environmental fate and human risk of herbicide orange and its associated dioxin. United States Air Force Rep. No. OEHL-TR-78-92. (Cited in NRCC 1981.)

6.3.14.4 Polychlorinated Biphenyls (PCBs)

6.3.14.4.1 Uses and Production

Polychlorinated biphenyls (PCBs) have been widely used in industrial applications because they have excellent thermal stability, strong resistance to both acid and base hydrolysis, general inertness, solubility in organic solvents, excellent dielectric properties, resistance to oxidation and reduction and nonflammability. They are also good lubricants and have high film strength (Gustafson 1970; Safe *et al*. 1982).

Commercial PCBs have been widely used in industry as heat-transfer fluids, hydraulic fluids, solvent extenders, plasticizers and dielectric fluids in electrical capacitors and transformers (Hutzinger *et al*. 1974). Other uses include flame retardants, additives, waterproofing agents, paints, surface coatings, adhesives, printing inks and pesticide extenders (Nisbet and Sarofim 1972; Roberts *et al*. 1978). Common articles containing PCBs are plastics, wrapping papers, carbon paper, printing inks, paints and tires (McNeely *et al*. 1979). Commercial PCBs may also contain polychlorinated dibenzofurans in varying amounts (Mitchell *et al*. 1984).

PCBs have been manufactured and used extensively since 1930 (Roberts *et al.* 1978). By 1970, about 31 000 t of PCBs were being sold annually in the United States (Hammond 1972). Cumulative total PCB production in North America up to 1971 was estimated to be 500 000 t; world production was estimated to be twice this amount (WHO 1976). The United States voluntarily reduced PCB production beginning in 1970 (Stratton and Sosbee 1976), and from 1972 to 1974 it averaged approximately 20 000 t·a^{-1}, with 16 500 t representing the annual domestic marketed consumption during that period (U.S. EPA 1980). The manufacture of PCBs was discontinued in the United States in 1977 (IARC 1978).

PCBs have also been manufactured in Czechoslovakia, France, Great Britain, Italy, Japan, Germany and the U.S.S.R., and they may still be made in most of these countries (Hutzinger *et al.* 1974; Health and Welfare Canada 1980).

PCBs used in Canada were imported almost exclusively from the United States (Health and Welfare Canada 1980). In the peak year 1970, 2450 t were imported from the United States, compared with 1590 t in 1974 (Environment Canada/Health and Welfare Canada 1976). On July 1, 1980, the use of chlorobiphenyls was totally prohibited as a constituent of any product, machinery or equipment manufactured in or imported into Canada (Environment Canada 1980). In Canada, PCBs are now used only in closed electrical equipment, such as transformers.

Names for polychlorinated biphenyls used by various manufacturers include Aroclor (McNeely *et al.* 1979); Clophen; Fenclor; Kanechlor; Phenochlor; Phenoclor (Safe *et al.* 1982); Pyralene; Santotherm; and Pyranol (Safe *et al.* 1982; Windholtz *et al.* 1983).

6.3.14.4.2 Sources and Pathways for Entering the Aquatic Environment

Among possible sources of PCBs entering the environment are the open burning or incomplete combustion of PCBs or wastes containing PCBs (Klein and Weisgerber 1976). Volatilization and transport as an aerosol followed by atmospheric deposition are probably responsible for the global dispersion of PCBs. The more highly chlorinated PCB species are less volatile than the lighter species (U.S. EPA 1979). Between 900 and 1800 t·a^{-1} escape into the atmosphere from plasticized materials, and about 3600 t·a^{-1} enter the waterways principally through sewage, leaching of lubricants, hydraulic and heat-transfer fluids and dumps and landfills (Hammond 1972). The discharge of PCBs in 26 Ontario municipal effluents to the Great Lakes was estimated to be 245 kg·a^{-1} (based on 1974 values) (Shannon *et al.* 1976). Recent surveys (1983-85) of sewage treatment plant effluents in Ontario have shown that, in most cases, PCB levels are not detectable. In those effluents where PCB concentrations can be measured, levels are very close to the detection limit (the low ng·L^{-1} range) (Ralston 1986). Approximately 29 t·a^{-1} of airborne PCBs are deposited to the Great Lakes. Wet deposition accounts for approximately 20-22% of the total atmospheric deposition (IJC 1981).

6.3.14.4.3 Environmental Concentrations

PCBs are among the most ubiquitous and persistent pollutants in the global ecosystem (Wyndham *et al.* 1976). Because of their limited solubility in water, PCBs are usually found in only trace concentrations in surface waters. Median concentrations of PCBs in the Great Lakes range from 1 to 10 ng·L^{-1} on a whole-lake basis. Concentrations are typically higher in the lower Great Lakes (e.g. Lake Erie, 2-10 ng·L^{-1}) than in the upper Great Lakes (e.g. Lake Superior, 1-2 ng·L^{-1}) (Eisenreich and Johnson 1983). PCB concentrations are usually highest in nearshore waters of the Great Lakes. For example, concentrations in nearshore waters of Lake Ontario typically range from 40 to 80 ng·L^{-1} (Simmons 1984). Median concentrations of PCBs in the sediments of the Great Lakes for the period of 1968 to 1975 range from approximately 3 to 100 ng·g^{-1}. The lower Great Lakes have a higher concentration (e.g. Lake Erie, 95 ± 114 ng·g^{-1}) than the upper Great Lakes (e.g. Lake Superior, 3.3 ± 5.7 ng·g^{-1}) (Eisenreich and Johnson 1983). Contaminated sediments resulting from industrial spills and discharges can contain significantly higher concentrations of PCBs. For example, Niagara River sediments were found to contain up to 2.7 mg·kg^{-1} near Queenston, Ontario (Kauss *et al.* 1983). PCB levels in surficial sediments of western Lake Erie (1985) and Collingwood Harbour of Lake Huron (1983) were 20-675 μg·kg^{-1} and 20-170 μg·kg^{-1}, respectively. These elevated levels are attributed to industrialization and sewage treatment plants (Ralston 1986).

PCBs are rarely detectable in Canadian drinking water; concentrations are generally expected to be less than 1 ng·L^{-1}. PCBs were not detected in drinking water in Ontario in 1975 and 1976 (Ontario Ministry of the Environment 1976). In 1980, PCBs were detected (0.02 μg·L^{-1}) in one of five treated water samples in St. Catharines. Samples of potable water from Niagara-on-the-Lake and Niagara Falls had nondetectable concentrations (detection limit 0.02 μg·L^{-1}) of PCBs (Kauss *et al.* 1983). PCBs were not detected (detection limit 0.02 μg·L^{-1}) in the treated drinking water of seven Ontario water treatment facilities surveyed in 1984 (Ontario Ministry of the Environment 1984).

In Canada, PCB residues have been found in lake trout, seal and polar bear from the Arctic; birds, coho salmon and other fish from inland aquatic ecosystems, including those associated with the Great Lakes; and birds' eggs from across Canada (Environment Canada/Health and Welfare Canada 1976; Roberts *et al.* 1978). The highest reported PCB residues are generally found in aquatic organisms from industrialized regions of the Great Lakes and the St. Lawrence River. Residues of PCBs in Atlantic coast fauna, although lower than those from inland regions, are generally higher than residues in Pacific coast fauna (Roberts *et al.* 1978). Residues in lake trout from Lakes Ontario, Michigan, Huron and Superior have, in general, declined between 1977 and 1982. For example, residues declined from 8.0 mg·kg^{-1} (wet weight) in 1977 to 3.7 mg·kg^{-1} (wet weight) in 1981 (IJC 1983). Residues of PCBs in spottail shiners (Suns 1985) and rainbow smelts have also declined. PCB residues in herring gull eggs from various colonies in the Great Lakes have also declined between 1973 and 1981 (IJC 1983).

NAQUADAT (1985) data reported only one region that had sampled for PCBs in Canadian surface waters. The Atlantic region sampled 10 times for PCBs prior to 1980 to give a range of 0.02-0.95 μg·L^{-1} (detection limit was not given) (NAQUADAT 1985).

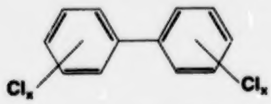


Figure 6-38. General structure of PCBs.

6.3.14.4.4 Forms and Fate in the Aquatic Environment

The empirical formula for polychlorinated biphenyls is $C_{12}H_{10-n}Cl_n$, where n may be any value from 1 to 10 (Figure 6-38) (Health and Welfare Canada 1980). There are 209 theoretically possible chlorinated biphenyl congeners (Cook 1972; Hutzinger *et al.* 1974) of which 194 have more than two chlorine atoms (Health and Welfare Canada 1980). Approximately 100 individual compounds have been identified in various PCB formulations (Hutzinger *et al.* 1974). PCBs with five or more chlorine atoms per molecule are referred to as "higher chlorobiphenyls", and are relatively more persistent in the environment than "lower chlorobiphenyls", which have four or fewer chlorine atoms (Roberts *et al.* 1978; U.S. EPA 1980). There are few data concerning the chemistry and biology of individual PCBs. Most data are for commercial PCB mixtures (Hutzinger *et al.* 1974; Peakall 1975; Environment Canada/Health and Welfare Canada 1976).

Individual PCBs vary widely in their physical and chemical properties according to the degree and position of chlorination (U.S. EPA 1979). Most PCBs are slightly soluble in water, and the solubility decreases with chlorine content. Some of the lower-chlorinated PCBs (e.g. some mono- and dichlorinated PCBs) are more soluble (Zitko 1970; Nisbet and Sarofim 1972; Mackay and Wolkoff 1973; Neely 1977; U.S. EPA 1979). Estimates of PCB solubility range from 2.7 to 15 000 $\mu g \cdot L^{-1}$ (U.S. EPA 1979); evidence suggests that solutions of PCBs in water are actually stable emulsions of PCB aggregations, and that true solubility of at least one commercial preparation is less than 0.1 $\mu g \cdot L^{-1}$ in fresh water (Schoor 1975). PCBs, with the exception of some lower-chlorinated compounds, have low volatility and are soluble in organic solvents, particularly hydrocarbons. They also have high dielectric constants and are inert towards acids, alkalis and other corrosive chemicals. They are also stable towards oxidation, and resist combustion at temperatures above their boiling points (Roberts *et al.* 1978). Temperatures in excess of 1000°C are required for their complete combustion (U.S. Interdepartmental Task Force on PCBs 1972; Hammond *et al.* 1972; Hutzinger *et al.* 1974).

Sorption to sediments is the predominant mechanism removing PCBs from the water column (U.S. EPA 1979). In aquatic environments, PCBs are usually found in much higher concentrations in sediments than in the overlying water (Crump-Wiesner *et al.* 1974; Dennis 1976; Young *et al.* 1976). PCBs have a high affinity for suspended solids, especially those high in organic carbon (Hamelink *et al.* 1971; U.S. EPA 1979). This is supported by their low water solubility and high octanol/water partition coefficients (calculated log P_{ow} values range from 3.76 for biphenyl to 8.26 for decachlorobiphenyl) (Miller *et al.* 1985).

The photolysis of PCBs has been demonstrated in non-aqueous solvents. Comparison of rates in oxygen-saturated and anaerobic solutions indicated that oxygen suppresses photolysis, apparently by acting as a free-radical quencher. Higher-chlorinated PCBs photodegrade faster than lower-chlorinated PCBs. From laboratory studies, it has been predicted that dechlorination via photolysis would be a very slow process in the aquatic environment (Safe *et al.* 1976; Bunce *et al.* 1978).

PCBs are extremely resistant to oxidation and hydrolysis (Hutzinger *et al.* 1974), and, hence, these processes are not expected to be significant in the aquatic environment (U.S. EPA 1979). Vapour pressures of PCBs have been found to be very low. For example, vapour pressures ranged from 1.8 Pa for biphenyl to 0.46 mPa for 2,2′,4,4′,5,5′-hexachlorobiphenyl (Burkhard *et al.* 1985). Volatilization of higher-molecular-weight PCBs from the water column is expected to be low. Half-lives of 9 to 12 h have been calculated (Mackay and Leinonen 1975); field studies and studies using sediment-water systems, however, indicate half-lives that are considerably longer (e.g. 1260 h) (Oloffs *et al.* 1972).

Individual PCBs vary widely in their susceptibility to biodegradation. PCBs with three or fewer chlorine atoms per molecule can be biodegraded by many organisms, whereas those with five or more chlorines are resistant to biodegradation and biotransformation. Tetrachlorobiphenyls are intermediate in their metabolic reactivity (U.S. EPA 1979; Furukawa 1982).

PCBs are soluble in the lipids of biological systems, and, therefore, tend to accumulate in fatty tissues, especially the higher chlorobiphenyls (Metcalf *et al.* 1975; Roberts *et al.* 1978). Bioconcentration factors of 200 000 and greater have been reported in fathead minnows (*Pimephales promelas*) (Duke 1971; Neely 1977) and pink shrimp (Klein and Weisgerber 1976), and up to 1 000 000 in other organisms (U.S. Interdepartmental Task Force on PCBs 1972; Nisbet 1976; Nebeker 1976; Hansen 1976). Therefore, relatively low levels of PCB contamination in aquatic systems can result in the accumulation of relatively high PCB levels in biota (Roberts *et al.* 1978). Extensive biomagnification in the aquatic food web is, however, apparently not a significant factor (Metcalf *et al.* 1975; Clayton *et al.* 1977).

6.3.14.4.5 References

Bunce, N.J., Y. Kumar and B.G. Brownlee. 1978. An assessment of the impact of solar degradation of polychlorinated biphenyls in the aquatic environment. Chemosphere 7: 155-164.

Burkhard, L.P., A.W. Andren and D.E. Armstrong. 1985. Estimation of vapour pressures for polychlorinated biphenyls. A comparison of eleven predictive models. Environ. Sci. Technol. 19: 506-507.

Clayton, J.R., Jr., S.P. Parlov and N.F. Breitner. 1977. Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning. Environ. Sci. Technol. 11: 676-682.

Cook, J.W. 1972. Some chemical aspects of polychlorinated biphenyls (PCBs). Environ. Health Perspect. 1: 3-13.

Crump-Wiesner, H.J., H.R. Feltz and M.L. Yates. 1974. Pesticides in water: a study of the distribution of polychlorinated biphenyls in the aquatic environment. Pestic. Monit. J. 8: 157-161. (Cited in U.S. EPA 1980.)

Dennis, D.S. 1976. Polychlorinated biphenyls in surface waters and bottom sediments of the major basins of the United States. *In* National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, Illinois. F.A. Ayers (compiler). Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/6-75-004. pp. 183-194. (Cited in U.S. EPA 1980.)

Duke, T.W. 1971. PCB Newsletter, 28 July. p. 8. (Cited in Health and Welfare Canada 1980.)

Eisenreich, S.J. and T.C. Johnson. 1983. PCBs in the Great Lakes: sources, sinks, burdens. *In* PCBs: Human and Environmental Hazards. F.M. D'Itri and M.A. Kamrin (eds.). Butterworth Publ., Boston, Massachusetts. pp. 49-75.

Environment Canada. 1980. Environmental Contaminants Act. Chlorobiphenyl Regulations No. 1, Amendment. The Canada Gazette Part II. Vol. 114(13): 2272-2274. Queen's Printer for Canada, Ottawa.

Environment Canada/Health and Welfare Canada. 1976. Background to the Regulation of Polychlorinated Biphenyls (PCB) in Canada. A Report of the Task Force on PCBs to the Environmental Contaminants Committee of Environment Canada and Health and Welfare Canada. Tech. Rep. 76-1. 169 pp. (Cited in Roberts *et al.* 1978.)

Furukawa, K. 1982. Microbial degradation of polychlorinated biphenyls. *In* Biodegradation and Detoxification of Environmental Pollutants. A.M. Chakrabarty (ed.). CRC Press, Inc., Boca Raton, Florida. pp. 33-57.

Gustafson, C.G. 1970. PCB's – prevalent and persistent. Environ. Sci. Technol. 4: 814-819. (Cited in U.S. EPA 1979.)

Hamelink, J.L., R.C. Waybrant and R.C. Ball. 1971. A proposal: exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Am. Fish. Soc. 100: 207-214. (Cited in U.S. EPA 1979.)

Hammond, A.L. 1972. Chemical pollution: polychlorinated biphenyls. Science 175: 155-156.

Hammond, P.B., I.C.T. Nisbet, A.F. Sarofim, W.H. Drury, N. Nelson and D.P. Rall. 1972. PCBs – environmental impact. Environ. Res. 5: 249-362.

Hansen, D.J. 1976. PCBs: Effects on and accumulation by estuarine organisms. *In* National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, Illinois. F.A. Ayer (compiler). Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/6-75-004. pp. 282-283. (Cited in Roberts *et al.* 1978.)

Health and Welfare Canada. 1980. Polychlorinated biphenyls (PCBs). *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 505-522.

Hutzinger, O., S. Safe and V. Zitko. 1974. The Chemistry of PCBs. CRC Press, Cleveland, Ohio.

IARC. 1978. Vol. 18. Polychlorinated Biphenyls and Polybrominated Biphenyls. International Agency for Research on Cancer Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva. p. 43.

IJC. 1981. Report on Great Lakes Water Quality – Appendix. Great Lakes Surveillance. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

IJC. 1983. Report on Great Lakes Water Quality – Appendix. Great Lakes Water Quality Board, International Joint Commission, Windsor, Ontario.

Kauss, P.B., K. Suns and A.F. Johnson. 1983. Monitoring of PCBs in water. *In* Physical Behaviour of PCBs in the Great Lakes. D. Mackay and S. Paterson (eds.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 385-409.

Klein, W. and I. Weisgerber. 1976. PCBs and environmental contamination. Environ. Qual. Saf. 5: 237-250. (Cited in Health and Welfare Canada 1980.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

Mackay, D. and A.W. Wolkoff. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7: 611-614.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Polychlorinated biphenyls. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 47-48.

Metcalf, R.L., J.R. Sanborn, P.-Y. Lu and D. Nye. 1975. Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra- and pentachlorobiphenyls compared with DDE. Arch. Environ. Contam. Toxicol. 3: 151-165.

Miller, M.M., S.P. Wasik, G.-L. Huang, W.-Y. Shiu and D. Mackay. 1985. Relationships between octanol-water partition coefficient and aqueous solubility. Environ. Sci. Technol. 19: 522-529.

Mitchell, M.F., H.A. McLeod and J.R. Roberts. 1984. Polychlorinated Dibenzofurans: Criteria for their Effects on Humans and the Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 22846. 243 pp.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Nebeker, A.V. 1976. Summary of recent information regarding effects of PCBs on freshwater organisms. *In* National Conference on Polychlorinated Biphenyls (November 19-21, 1975, Chicago, Illinois). F.A. Ayer (compiler). Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/6-75-004. pp. 284-291. (Cited in Roberts *et al.* 1978.)

Neely, W.B. 1977. A material balance study of polychlorinated biphenyls in Lake Michigan. Sci. Total Environ. 7: 117-129.

Nisbet, I.C.T. 1976. Criteria Document for PCBs. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/9-76-021.

Nisbet, I.C.T. and A.F. Sarofim. 1972. Rates and routes of transport of PCBs (polychlorinated biphenyls) in the environment. Environ. Health Perspect. 1: 21-38. (Cited in Health and Welfare Canada 1980.)

Oloffs, P.C., L.J. Albright and S.Y. Szeto. 1972. Fate and behaviour of five chlorinated hydrocarbons in three natural waters. Can. J. Microbiol. 18: 1393-1398.

Ontario Ministry of the Environment. 1976. Polychlorinated Biphenyls in the Ontario Environment. Toronto, Ontario.

Ontario Ministry of the Environment. 1984. Drinking Water Survey of Selected Municipalities in the Niagara Area and Lake Ontario, November. Toronto, Ontario.

Peakall, D.B. 1975. PCBs and their environmental effects. CRC Crit. Rev. Environ. Control 5: 469-508.

Ralston, J.G. 1986. Personal communication. Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario.

Roberts, J.R., D.W. Rodgers, J.R. Bailey and M.A. Rorke. 1978. Polychlorinated Biphenyls: Biological Criteria for an Assessment of Their Effects on Environmental Quality. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 16077. 172 pp.

Safe, S., N.J. Bunce, B. Chittin, O. Hutzinger and L.O. Ruzo. 1976. Photodecomposition of halogenated aromatic compounds. *In* Identification and Analysis of Pollutants in Water. L.H. Keith (ed.). Ann Arbor Science Publ., Ann Arbor, Michigan. pp. 35-47.

Safe, S., A. Parkinson, L. Robertson, L. Safe and S. Bandiera. 1982. Polychlorinated biphenyls: Effects of structure on biologic and toxic activity. *In* Workshop on the Combined Effects of Xenobiotics (June 22-23, 1981, Ottawa, Ontario). H.F. Stich, H.W. Leung and J.R. Roberts (eds.). Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18978. pp. 151-176.

Schoor, W.P. 1975. Problems associated with low-solubility components in aquatic toxicity tests: theoretical model and solubility characteristics of Aroclor 1254 in water. Water Res. 9: 937-944.

Shannon, E.E., F.J. Ludwig and I. Valdmanis. 1976. Polychlorinated Biphenyls in Municipal Wastewaters: An Assessment of the Problem in the Canadian Lower Great Lakes. Canada/Ontario Agreement on Great Lakes Water Quality, Ottawa. Res. Rep. No. 49.

Simmons, M.S. 1984. PCB contamination in the Great Lakes. *In* Toxic Contaminants in the Great Lakes. J.O. Nriagu and M.S. Simmons (eds.). John Wiley & Sons, New York. pp. 287-309.

Stratton, C.L. and J.B. Sosbee, Jr. 1976. PCB and PCT contamination of the environment near sites of manufacture and use. Environ. Sci. Technol. 10: 1229-1233. (Cited in Health and Welfare Canada 1980.)

Suns, K. 1985. Temporal Trends and Spatial Distribution of Organochlorine and Mercury Residues in Great Lakes Spottail

Shiners. Unpublished report. Ontario Ministry of the Environment, Toronto, Ontario.

U.S. EPA. 1979. Polychlorinated biphenyls. *In* Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction, Technical Background, Metals and Inorganics, Pesticides, Polychlorinated Biphenyls. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 36-1 to 36-18.

U.S. EPA. 1980. Ambient Water Quality Criteria for Polychlorinated Biphenyls. Office of Water Regulations and Standards Criteria, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-068.

U.S. Interdepartmental Task Force on PCBs. 1972. PCBs and the Environment. Springfield, Virginia. Natl. Tech. Inf. Serv. Rep. ITF-PCB-72-1. 179 pp.

WHO. 1976. Polychlorinated Biphenyls and Terphenyls. Environmental Health Criteria 2, World Health Organization, Geneva.

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

Wyndham, C., J. Devenish and S. Safe. 1976. The *in vitro* metabolism, macromolecular binding and bacterial mutagenicity of 4-chlorobiphenyl, a model PCB substrate. Res. Commun. Chem. Pathol. Pharmacol. 15: 563-570. (Cited in Health and Welfare Canada 1980.)

Young, D.R., D.J. McDermott and T.C. Heeson. 1976. Marine inputs of polychlorinated biphenyls off southern California. *In* National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, Illinois. F.A. Ayers (compiler). Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. EPA-560/6-75-004. pp. 199-208. (Cited in U.S. EPA 1980.)

Zitko, V. 1970. Polychlorinated biphenyls (PCB) solubilized in water by nonionic surfactants for studies of toxicity to aquatic animals. Bull. Environ. Contam. Toxicol. 5: 279-285.

6.3.15 Resin Acids

6.3.15.1 Uses and Production

Oleoresins and tall oil, which contain resin acids, are used extensively in the manufacture of tar, pitch, turpentine, rubber, adhesives, coatings and inks. Rosin is used for paper sizing in the pulp and paper industry. World production of rosin between 1960 and 1979 was 9.07 x 10^8 kg (Enos *et al.* 1970).

Rosin and tall oil fatty acids are produced in Ontario, whereas tall oil is produced in Ontario, British Columbia, Saskatchewan and Alberta. Canadian production, importation, consumption and exportation of these compounds are presented in Table 6-154 (CORPUS Information Services 1981).

6.3.15.2 Sources and Pathways for Entering the Aquatic Environment

Numerous resin acids and resin acid salts have been identified in mechanical pulping effluents, unbleached whitewater, woodroom wastes, bleached kraft whole mill effluents, sulphite effluents and paper mill effluents (Hemingway and Greaves 1973; Leach and Thakore 1976).

Information on concentrations in the final effluents discharged to the aquatic environment are limited. Resin acids and fatty acids were detected in the final effluent of a pulp and paper plant located on the St. Lawrence River at Cornwall, Ontario. The concentration ranges for each resin acid and fatty acid, based on three samples taken for each, are presented in Table 6-155 (Environment Canada 1984).

6.3.15.3 Environmental Concentrations

Information on concentrations of resin and fatty acids in Canadian surface waters is unavailable. Sampling results for oleoresins, tall oil, rosin, resin acids and fatty acids are not reported in NAQUADAT (1985).

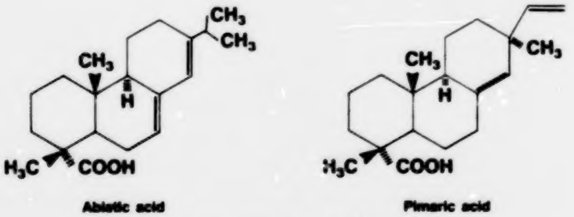
6.3.15.4 Forms and Fate in the Aquatic Environment

Resin acids are unsaturated, tricyclic monocarboxylic acids that are present in oleoresin (Rogers *et al.* 1969; Swan 1973), a composition of hydrophobic material of conifers, and in tall oil (Rogers and Harris 1970; Enos *et al.* 1970), a resin containing by-products of the kraft pulping process.

Approximately 70% of the acute toxicity to fish of mechanical pulping effluents has been attributed to the acidic fraction of the effluents. The major toxic constituent in the acidic fraction was found to contain seven resin acids: dehydroabietic, palastric, abietic, isopimaric, pimaric, sandaracopimaric and neoabietic acids (Leach and Thakore 1976).

Abietic acid (1,2,3,4,4a,4b,5,6,10,10a-decahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxylic acid) (Figure 6-39) has a molecular formula of $C_{20}H_{30}O_2$, a molecular weight of 302.44 and a melting point of 172-175°C. Pimaric acid (7-ethenyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-decahydro-1,4a,7-trimethyl-1-phenanthrenecarboxylic acid) (Figure 6-39) has the same molecular formula and molecular weight as abietic acid, but melts at 217-219°C. Resin acids are normally insoluble in water, but their salts are soluble. The acids are soluble in various organic solvents and in dilute sodium hydroxide via formation of sodium salts (Windholtz *et al.* 1983).

Although acutely toxic, resin acid salts may be microbially degraded in activated sludge and surface waters. The incubation of resin acids in activated sludge and surface water at 27°C resulted in degradation to nondetectable levels in 12-40 h after an initial lag period of 18-28 h. At a lower temperature (12°C), the lag phase increased to 80-140 h before degradation to nondetectable levels in 20-30 h (Hemingway and Greaves 1973). Pimaric and isopimaric acids were found to be resistant to microbial attack, with detectable levels after 164 h of incubation at 12°C (Hemingway and Greaves 1973).



Abietic acid

Pimaric acid

Figure 6-39. Abietic and pimaric acids.

6.3.15.5 References

CORPUS Information Services. 1981. Rosin. Tall oil fatty acids. Tall oil. CPI Product Profiles. Don Mills, Ontario.

Table 6-154. Production, Consumption, Importation and Exportation of Rosin, Tall Oil Fatty Acids and Tall Oil in Canada

Compound	Year	Amount (t)			
		Production	Consumption	Importation	Exportation
Rosin	1979	3 500	13 000	9500	0
	1980	3 500	13 000	9500	0
Tall oil fatty acids	1979	4 000	8 800	4800	0
	1980	4 500	8 800	4300	0
Tall oil	1979	51 000	20 500	600	31 000
	1980	57 000	20 500	500	37 000

Source: CORPUS Information Services 1981.

Table 6-155. Concentration Ranges for Resin Acids Detected in the Final Effluent of a Pulp and Paper Plant at Cornwall, Ontario

Compound	Concentration range ($\mu g \cdot L^{-1}$)
Resin acids	
Pimaric	140-160
Isopimaric	80-111
Neoabietic	410-490
Abietic	1110-1190
Dehydroabietic	40-90
Fatty acids	
Palmitic (hexadecanoic)	310-460
Stearic (octadecanoic)	80-130
Oleic (octadecenoic)	130-310
Linoleic (octadecadienoic)	660-3720
Linolenic (octadecatrienoic)	30-70

Source: Environment Canada 1984.

Enos, H.I., G.C. Harriss and G.W. Hedrick. 1970. Rosin and rosin derivatives. Encyclopedia of Chemical Technology. Interscience Publ., New York. p. 475. (Cited in Health and Welfare Canada 1980.)

Environment Canada. 1984. 1980-1981 Cornwall Industrial Survey. Draft. Pollution Control Division, Environmental Protection Service – Ontario Region, Toronto, Ontario.

Health and Welfare Canada. 1980. Resin acids. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 537-540.

Hemingway, R.W. and H. Greaves. 1973. Biodegradation of resin acid sodium salts. Tappi 56(12): 189-192.

Leach, J.M. and A.N. Thakore. 1976. Toxic constituents in mechanical pulping effluents. Tappi 59(2): 129-132.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Rogers, I.H. and A.G. Harris. 1970. Potential Tall Oil Yield from British Columbia Interior Pine and Spruce. Vancouver, British Columbia. Forest Products Laboratory Information Report VP-X-62. (Cited in Health and Welfare Canada 1980.)

Rogers, I.H., A.G. Harris and L.R. Rozon. 1969. The Wood Resin Content and Fatty Acid Composition of Five British Columbia Plywood Conifers. Vancouver, British Columbia. Forest Products Laboratory Information Report VP-X-57. (Cited in Health and Welfare Canada 1980.)

Swan, E.P. 1973. Resin Acids and Fatty Acids of Canadian Pulpwoods – A Review of the Literature. Environment Canada Forestry Service Information Report VP-X-115. (Cited in Health and Welfare Canada 1980.)

Windholtz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds.). 1983. The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 10th edition. Merck and Co., Inc., Rahway, New Jersey.

6.3.16 Surfactants

6.3.16.1 Uses and Production

Surfactants, also called surface active agents or wetting agents, are organic chemicals that reduce surface tension in water and other liquids (McNeely *et al.* 1979; Dean and Bradley 1984; Dean 1985). The most familiar uses for surfactants are in soaps, laundry detergents, dishwashing liquids and shampoos. Other important uses are in the many industrial applications for surfactants in lubricants, emulsion polymerization, textile processing, mining flocculants, petroleum recovery, wastewater treatment and many other products and processes (Dean 1985). Surfactants and surfactant intermediates produced, imported and used in Canada are presented in Table 6-156. Importation data for industrial surfactants are presented in Table 6-157.

There are several hundred compounds that can be used as surfactants and are usually classified by their ionic behaviour in solutions: anionic, cationic, nonionic or amphoteric (zwitterionic) (Dean and Bradley 1984). Each surfactant class has its own specific properties, presented in Table 6-158, along with examples of commonly used commercial and industrial surfactants (Tobin and Anthony 1975; Dean and Bradley 1984; Dean 1985).

6.3.16.2 Sources and Pathways for Entering the Aquatic Environment

There are many sources of surfactants that are discharged into natural waterways. Industrial sources include textile and leathering processes, dyeing and finishing, surfactant manufacture and detergent formulation. Surfactants are also used by laundries and households, and, therefore, are found in discharges from sewage treatment plants. They also have agricultural applications in pesticides, as diluents and dispersants (McNeely *et al.* 1979).

Limited information is available on surfactant concentrations in Canada. This is perhaps because of the high biodegradability and low toxicity of the various surfactants available on today's markets (Tobin and Anthony 1975; McNeely *et al.* 1979). In a 1979 survey of textile mills in Canada that examined, among other processes, the efficiency of their effluent treatment process, three of six mills sampled reported final effluent concentrations containing nonionic surfactants.

Table 6-156. Production, Consumption, Importation and End Uses of Surfactants and Surfactant-related Substances in Canada

Compound	Year	Production (t)	Consumption (t)	Importation (t)	End uses
Detergent alcohols ($C_{12}-C_{18}$ fatty alcohols)	1978	0	6 700	6 700	Ethoxylates, sulphates, textile specialties
Detergent alkylate	1979 1980	0 0	25 000 26 000	27 300 23 500	Light- and heavy-duty liquids, heavy-duty powders, all-purpose cleansers, scouring cleansers
Ethanolamines (mono, di, triethanolamines, hydroxyethylamines)	1979 1980	10 300 10 600	12 500 13 400	2 200 3 900	Surfactants, gas adsorbent, cleaners, detergents, concrete additives
Ethoxylated alcohols (linear alcohol ethoxylates, etc.)	1979 1980	10 000 11 000	17 000 17 300	6 800 6 300	Gypsum board, demulsifiers, pulp and paper specialties, textile specialties, ether sulphates, heavy-duty detergents
Fatty acids, distilled ($C_{12}-C_{22}$ fatty acids)	1978	44 000	50 000	6 900	Cleaners, mining chemicals, surfactants, alkyl resins, alkyds, metal stearates, rubber compounding, cutting oils, soaps, niobium flotation, emulsion polymerization, epoxy plasticizers, phosphates, polishes
Fatty amines (primary, secondary, tertiary amines, diamines)	1979 1980	6 000 6 000	10 500 10 800	4 500 4 800	Corrosion inhibitors, ethoxylates, quaternaries, potash flotation, asphalt emulsions, iron ore flotation, niobium flotation, oil and fuel additives
Fatty-alcohol sulphates (sodium lauryl sulphate, sodium lauryl ether sulphates, etc.)	1978	19 000	20 500	1 500	Shampoos, cleaners, vinyl emulsions, wallboard, detergents, toiletries, SB latex, dental cream
Nonylphenol	1983 1984	5 000 5 200	5 900 5 400	400 400	Nonylphenol ethoxylates, tackifiers, lube-oil additives, resins, phosphite stabilizers
Polyacrylamides (PAM)	1978 1979	500 500	4 500 5 000	3 700 4 300	Retention aid, industrial water treatment, tailings flocculant, water treatment, sewage flocculant, flocculant, mining flocculant, uranium mining

Sources: CORPUS Information Services 1979, 1980, 1981, 1985.

Table 6-157. Importation of Various Industrial Surfactants into Canada

	Amount (t)	
Surfactant	1981	1982
Sulphate-based surfactants	719	683.4
Olefin sulphonate-based surfactants	31.4	1.7
Sulphonate-based surfactants	4502.1	3835.6
Anionic surfactants (group not specified)	1625.9	1227.4
Ethoxylated alcohol surfactants	3095.2	2145.6
Phenol-based surfactants	234.1	360.5
Amide-based surfactants	851.5	539.8
Amine-based surfactants	588.5	1499.7
Fatty acid ester-based surfactants	508.6	418.8
Sorbitan derivative surfactants	314.1	213.1
Nonionic surfactants (group not specified)	1949.9	1849.5
Cationic surfactants	851.2	993.7
Ampholytic surfactants	499.7	464
Compounded surfactants	8534	9109

Source: Statistics Canada 1983.

Nonionic surfactants are the common class of surfactant used, and this was the only class sampled in this survey. Concentrations for the nonionic surfactants are presented in Table 6-159 (Environment Canada 1982).

6.3.16.3 Environmental Concentrations

Information on concentration ranges for surfactants in Canadian surface waters is limited. No sampling results for anionic or nonionic surfactants were reported in NAQUADAT (1985). Concentrations, however, of some surfactants were reported in NAQUADAT (1985), and are presented in Table 6-160. Also, the Atlantic region reported a concentration range for resin acid soaps of nondetectable (0.1 mg·L^{-1}) to 10 mg·L^{-1}, based on 328 samples taken prior to 1980 (NAQUADAT 1985). The information on resin acids relates to these compounds as components of pulpmill effluents, not as intentionally used surfactants.

6.3.16.4 Forms and Fate in the Aquatic Environment

Surfactants are compounds that are composed of both hydrophilic and hydrophobic or lipophilic groups. Because of their dual hydrophilic and hydrophobic nature, surfactants tend to concentrate at the interfaces of aqueous mixtures; the hydrophilic part of the surfactant orients itself towards the aqueous phase, and the hydrophobic part orients itself away from the aqueous phase into the second phase. This preferential concentration at interfaces is responsible for surfactants' ability to stabilize emulsions, thereby leading to their utility in preventing coagulation and settling (Garrett 1972; McNeely *et al.* 1979; Datyner 1983; Tadros 1984).

The hydrophobic portion of a surfactant molecule is generally derived from a hydrocarbon containing 8 to 20 carbon atoms (e.g. fatty acids, paraffins, olefins, alkylbenzenes). The hydrophilic portion may either ionize in aqueous solution (cationic, anionic) or remain un-ionized (nonionic). Surfactants

Table 6-158. General Properties of Major Surfactant Classes and Examples of Major Commercial and Industrial Surfactants

Characteristic	Anionic	Cationic	Nonionic	Amphoteric
Electric charge	Negative	Positive	None	Positive in acid Negative in alkali
Detergency	Medium to high	Low	High	Low
Cost	Low to medium	High	Low to medium	High
Mildness to skin	Moderate	Harsh	Moderate to harsh	Mild
Foam	High	Low to medium	Low to medium	Low to medium
Incompatibilities	With cationics	With anionics	None	Depends on pH
Special properties		Germicidal conditioning		Often low eye irritation
Commercial and domestic examples	Sodium linear alkylbenzene sulphonate (LABS), sodium lauryl sulphate, sodium lauryl ether sulphates, alcohol ethoxysulphates, alkyl sulphates[1], linear alkylbenzene sulphonates[1], alcohol ethoxysulphates[1], fatty alcohol sulphates and alcohol ether sulphonates, alpha olefin sulphonates	Stearalkonium chloride, benzalkonium chloride, bis(hydrogenated tallow alkyl) dimethylammonium chloride	Dodecyl dimethylamine oxide, Coco diethanol-amide, alcohol ethoxylates[1], linear primary alcohol polyethoxylate[1], fatty acid diethanolamides[1], secondary alcohol polyethoxylate[1], polyethoxylate-polypropoxylate block polymers[1]	Cocoampho-carboxyglycinate, cocamidopropylbetaine
Major industrial examples	Petroleum sulphonates, linosulphonates, naphthalene sulphonates, branched alkylbenzene sulphonates, linear alkylbenzene sulphonates, alcohol sulphates, alcohol ether sulphates, phosphates, carboxylic acid salts	Quaternary ammonium compounds, amine compounds	Alkylphenol ethoxylates, alcohol ethoxylates, EO/PO polyol block polymers, polyethylene glycol esters, fatty acid alkanolamides	Betaines, imidazolines

[1] Most widely used commercial and domestic surfactants in Canada (McNeely *et al.* 1979).

Sources: Tobin and Anthony 1975; Dean and Bradley 1984; Dean 1985.

Table 6-159. Concentrations of Nonionic Surfactants (Linear Alcohol and Ethoxylated Nonylphenol) in the Final Effluent from Three Textile Mills

	Concentration in final effluent ($mg \cdot L^{-1}$)	
Textile mill type	Linear alcohol	Ethoxylated nonylphenol
Knit fabric finishing mill	10	20
Woven fabrics finishing mill	330	170
Woven fabrics finishing mill	1400	400

Source: Environment Canada 1982.

Table 6-160. Environmental Concentration Ranges for Surfactants in Canadian Surface Waters

Region	Concentration range[1] ($mg \cdot L^{-1}$)	Number of samples	Sampling year(s)
Pacific	ND[2]	116	Prior to 1980
Western	ND-0.04	241	1980-1985
Central	ND-6.3	431	Prior to 1980
Atlantic	ND	80	Prior to 1980

[1] Detection limit is 0.5 $mg \cdot L^{-1}$ (for Methylene Blue Active Substances).
[2] ND = not detected.

Source: NAQUADAT 1985.

and surfactant mixtures may also be amphoteric or zwitterionic (Datyner 1983; Tadros 1984). Examples of the various surfactant groups include anionic (linear alkylbenzene sulphonate); cationic (dialkyl dimethyl ammonium compounds); nonionic (nonylphenol ethoxylates); and zwitterionic (dimethyl dodecylamine propane sulphonate) (Tadros 1984).

Surfactants, because of their hydrophilic nature, tend to be water-soluble to some degree. Depending upon the specific chemical, solubility varies from very soluble (e.g. some anionic surfactants) to insoluble (e.g. some cationic surfactants) (Lewis and Wee 1983). Anionic surfactants are not appreciably sorbed by inorganic solids (Beveridge and Pickering 1983). On the other hand, cationic surfactants are strongly sorbed by solids, particularly clays (Lewis and Wee 1983). Significant sorption of both anionic and nonionic surfactants has been observed in activated sludge (Urano and Saito 1984) and organic river sediments (Urano *et al.* 1984). Depending upon the nature of their hydrophobic moieties, nonionic surfactants may be sorbed onto surfaces (Law and Kunze 1966). Cyclohexane/water partition coefficients (P_{cw}) for two nonionic surfactants, hexaoxyethylene nonylphenyl ether, and octaoxyethylene nonylphenyl ether, were calculated to be approximately 2.6 and 1.9, respectively (Harusawa *et al.* 1980). Some surfactants have been found to alter the sorption to surfaces of coexisting chemical species, such as metals. For example, the adsorption by clays of copper, zinc, cadmium and lead was significantly reduced in the presence of small amounts of cationic surfactants. This decreased adsorption was especially pronounced with montmorillonite suspensions compared with illite and kaolinite. However, cationic surfactants increased metal loss from aqueous solution because of enhanced precipitation of the metal that remained nonadsorbed to the clay. Depending upon the particular compound, nonionic surfactants tended to remove metals from solution via micelle formation (Beveridge and Pickering 1983).

In general, surfactants in modern-day use are considered to be biodegradable under conditions of efficient sewage treatment. The rates of degradation depend partially on chemical structure (Reiff *et al.* 1979; Gode 1984). Surfactants containing linear hydrophobes are more readily biodegraded than those containing branched hydrophobes (Scharer *et al.* 1979; Kravetz 1983). Nonylphenol and some of its ethoxylates are not readily degraded during sewage treatment. For example, nonylphenol, at an initial concentration of 1 mg·L^{-1}, was degraded 0 and 45% after incubation in normal and activated sewage (Verschueren 1983). Nonylphenolmono- and diethoxylates have been detected as major constituents in biologically treated wastewater effluents (Giger *et al.* 1981; Schaffner *et al.* 1982; Stephanou *et al.* 1982) and in river waters (Ahel *et al.* 1984). In many cases, degradation products appear to be less acutely toxic to aquatic organisms than is the parent compound (Dolan and Hendricks 1976; Kimerle and Swisher 1977).

Little information is available on the accumulation of surfactants in aquatic biota because of their apparent rapid biodegradation. Steady-state bioaccumulation factors of 20 in gill tissue and blood, 100 in liver and kidney and 800 in gall bladder were calculated for exposure of cod (*Gadus morrhua* L.) to 5 mg·L^{-1} nonylphenol ethoxylate (a nonionic surfactant) at 11°C. Elimination of the surfactant appeared, however, to be rapid (Granmo and Kollberg 1976). Whole-body bioconcentration factors of 32 (well water) and 13 (river water) were calculated for exposure of bluegill sunfish (*Lepomis macrochirus*) to approximately 20 μg·L^{-1} of ditallow dimethyl ammonium chloride (a cationic surfactant). The lower bioconcentration factor of bluegill sunfish in river water was attributed to the presence of suspended solids and dissolved anionic organic materials. Elimination was rapid, with almost complete loss in 14 d (Lewis and Wee 1983).

Surfactants may also alter the pharmacokinetics and toxicity of some coexisting pollutants. For example, linear alkylbenzene sulphonate (an anionic surfactant) increased the uptake of cadmium and increased its transfer through the perfused gills of a rainbow trout (*Salmo gairdneri*). Nonionic surfactants had no effect (Pärt *et al.* 1985). The enhanced toxicity of heavy metals in the presence of anionic surfactants has been identified (Calamari and Marchetti 1973).

6.3.16.5 References

Ahel, M., W. Giger, E. Molnar-Kubica and C. Schaffner. 1984. Organic micropollutants in surface waters of the Glatt Valley, Switzerland. *In* Analysis of Organic Micropollutants in Water. G. Angeletti and A. Bjorseth (eds.). D. Reidel Publ. Co., Dordrecht, Holland. pp. 91-109.

Beveridge, A. and W.F. Pickering. 1983. The influence of surfactants on the adsorption of heavy metal ions by clays. Water Res. 17: 215-225.

Calamari, D. and R. Marchetti. 1973. The toxicity of mixtures of metals and surfactants to rainbow trout (*Salmo gairdneri*). Water Res. 7: 1453-1464.

CORPUS Information Services. 1979. Fatty-alcohol sulfates. Fatty acids, distilled. Detergent alcohols. CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1980. Detergent alkylate. Polyacrylamides. CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1981. Fatty amines. Ethoxylated alcohols. Ethanolamines. CPI Product Profiles. Don Mills, Ontario.

CORPUS Information Services. 1985. Nonylphenol. CPI Product Profiles. Don Mills, Ontario.

Datyner, A. 1983. Surfactants in Textile Processing. Marcel Dekker, Inc., New York. 212 pp.

Dean, J. 1985. To stay on top of constantly shifting markets, producers must zero in on research and technical service. Chem. Week 136(20): SAS 3 to SAS 34.

Dean, J. and R. Bradley. 1984. Part I, Industrial surfactants: A complex market, buffeted by shifting trends in technology, raw materials, sales strategies. Chem. Week 135(24): SAS 3 to SAS 34.

Dolan, J.M., III and A.C. Hendricks. 1976. The lethality of an intact and degraded LAS mixture to bluegill sunfish and a snail. J. Water Pollut. Control Fed. 48: 2570-2577.

Environment Canada. 1982. Survey of Textile Wet Processing and Pollution Abatement Technology. Environmental Protection Service, Ottawa. Economic and Technical Review Report EPS 3-WP-82-5. 116 pp.

Garrett, H.E. 1972. Surface Active Chemicals. Pergamon Press, Oxford, U.K. 167 pp.

Giger, W., E. Stephanou and C. Schaffner. 1981. Persistent organic chemicals in sewage effluents.1. Identification of nonylphenols and nonylphenolethoxylates by glass capillary gas chromatography/mass spectrometry. Chemosphere 10: 1253-1263.

Gode, P. 1984. Reduction of surfactant concentrations in static fish tests compared with biodegradation rates in the OECD screening test. Chemosphere 13: 933-938.

Granmo, A. and S. Kollberg. 1976. Uptake, pathways and elimination of a nonionic surfactant in cod (*Gadus morrhua* L.). Water Res. 10: 189-194.

Harusawa, F., T. Saito, H. Nakajima and S. Fukushima. 1980. Partition isotherms of nonionic surfactants in the water-cyclohexane system and the type of emulsion produced. J. Colloid Interface Sci. 74: 435-440.

Kimerle, R.A. and R.D. Swisher. 1977. Reduction of aquatic toxicity of linear alkylbenzene sulphonate (LAS) by biodegradation. Water Res. 11: 31-37.

Kravetz, L. 1983. Biodegradation of nonionic surfactants – alcohol ethoxylates vs. nonylphenol ethoxylates. Text. Chem. Color. 15(4): 57/23 to 28/62.

Law, J.P. and G.W. Kunze. 1966. Reactions of surfactants with montmorillonite: adsorption mechanisms. Soil Sci. Soc. Am. Proc. 30: 321-327.

Lewis, M.A. and V.T. Wee. 1983. Aquatic safety assessment for cationic surfactants. Environ. Toxicol. Chem. 2: 105-118.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Surfactants. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 58-59.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Pärt, P., O. Svanberg and E. Bergström. 1985. The influence of surfactants on gill physiology and cadmium uptake in perfuse rainbow trout gills. Ecotoxicol. Environ. Saf. 9: 135-144.

Reiff, B., R. Lloyd, M.J. How, D. Browns and J.S. Alabaster. 1979. The acute toxicity of eleven detergents to fish: results of an interlaboratory exercise. Water Res. 13: 207-210.

Schaffner, C., E.Stephanou and W. Giger. 1982. Determination of nonylphenols and nonylphenolethoxylates in secondary sewage effluents. *In* Analysis of Organic Micropollutants in Water. A. Bjorseth and G. Angeletti (eds.). D. Reidel Publ. Co., Dordrecht, Holland. pp. 320-324.

Scharer, D.H., L. Dravety and J.B. Carr. 1979. Biodegradation of nonionic surfactants. Tappi 62(10): 75-78.

Statistics Canada. 1983. Imports: Merchandise Trade, Commodity Detail 1982. Catalogue No. 65-207.

Stephanou, E. and W. Giger. 1982. Persistent organic chemicals in sewage effluents. 2. Quantitative determination of nonylphenol and nonylphenolethoxylates by glass capillary chromatography. Environ. Sci. Technol. 16: 800-805.

Tadros, Th.F. (ed.). 1984. Surfactants. Academic Press, London. 342 pp.

Tobin, R.S. and D.H.J. Anthony. 1975. Testing the Biodegradability of Nonionic Surfactants by the O.E.C.D. Dynamic Simulation Test. Unpublished report. Canada Centre for Inland Waters, Burlington, Ontario. 21 pp.

Urano, K. and M. Saito. 1984. Adsorption of surfactants on microbiologies. Chemosphere 13: 285-292.

Urano, K., M. Saito and C. Murata. 1984. Adsorption of surfactants on sediments. Chemosphere 13: 293-300.

Verschueren, C. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

6.4 PHYSICAL PARAMETERS

6.4.1 Colour

6.4.1.1 Introduction

The colour of water that is perceived is made up of unabsorbed light rays, from the incident light, which pass out of the water. Pure water would absorb all the light components and appear nearly black, but this is not seen in natural bodies of water. Lakes that contain very small quantities of suspended material appear blue, probably as a result of scattering of light by water molecules in motion. In some cases, very finely divided suspended matter may produce a green colour (Hutchinson 1957).

Colour and turbidity determine light transmission in water, and "regulate" biological processes within the body of water. Both characteristics give some qualitative indication of the productivity of the water when viewed from above (Reid and Wood 1976).

There are two measures of colour in water: true and apparent. The true colour of natural water is the colour of water from which turbidity has been removed (i.e. filtered or centrifuged water) (Reid and Wood 1976). Apparent colour is determined on the original sample without filtration or centrifugation.

Natural minerals give true colour to water; for example, calcium carbonate in limestone regions gives a greenish colour, and ferric hydroxide, red. Organic substances, tannins, lignin and humic acids from decaying vegetation also give true colour to water (Wetzel 1975; Reid and Wood 1976).

Apparent colour is usually caused by the interplay of light on suspended particulates, and the presence of coloured particulates. The reflection of the bottom or sky is also a factor. When the density of particulate matter suspended in the water (collectively called seston) becomes great, a seston colour can be seen. This can be from inorganic materials, such as clays, but usually it is associated with suspended algae, pigmented bacteria or microcrustaceans (Hutchinson 1957; Wetzel 1975).

Table 6-161. Environmental Ranges of Colour in Canadian Surface Waters

Region	Range[1] (rel. units)	Number of samples	Sampling year(s)
Pacific	<5 and 40	2	Prior to 1980
Western	5-240	1976	1980-1983
Central	5-200	142	1980-1981
Atlantic	65-130	11	1980

[1] True colour.

Source: NAQUADAT 1985b.

Blue-green algae give an overall appearance of dark green or blue-green. Yellow-brown colours are produced by diatoms; red and purple colours can also occur, for example, when large numbers of zooplankton, such as *Daphnia* or diaptomid copepods, are present. With *Euglena sanguinea*, *Chromulina* and other blue-green algal blooms, the organisms may be associated with the surface film, and the resultant colouration should be termed neuston colour instead of seston colour (Hutchinson 1957; Wetzel 1975).

Some lakes have an increase of colour with depth, and this is suggested as being because of the organic substances derived from the bottom sediments as well as increased phytoplankton populations supported by such substances (Reid and Wood 1976).

6.4.1.2 Measurement of Colour

One of the methods for measuring colour that is used in Canada and the U.S.A. is the platinum-cobalt scale. The method involves the comparison of lake waters in a series of dilutions of a solution of potassium chloroplatinate (K_2PtCl_4) and crystalline cobaltous chloride ($CoCl_2{\cdot}H_2O$) (Environment Canada 1979). The units are called platinum-cobalt units, based on 1 $mg{\cdot}L^{-1}$ Pt as a standard, and range quite widely from very low in clear waters to over 300 units in very dark bog water (Reid and Wood 1976).

Another method is the total absorbance colour (TAC). This is determined by measuring the integrated absorbance of the filtered sample (pH adjusted to 7.6) between 400 and 700 nm. One unit of TAC colour may be defined as the colour produced by 2 $mg{\cdot}L^{-1}$ Pt in the form of the chloroplatinate ion. The units range from 1 to 250 (British Columbia Ministry of Environment 1976).

A third method measures the true colour of receiving water and pulp mill effluents. The sample is filtered, the pH adjusted to 7.6 and the absorbance measured at 465 nm. The colour is measured against a platinum-cobalt standard, and the results are reported relative to the Hazen colour scale (NAQUADAT 1985a).

Environmental ranges of colour in Canadian surface waters are presented in Table 6-161.

6.4.1.3 References

British Columbia Ministry of Environment. 1976. A Laboratory Manual for the Chemical Analysis of Waters, Wastewaters, Sediments and Biological Tissues. 2nd edition. Computed by N.R. McQuaker. Water Resources Service, Victoria, British Columbia.

Environment Canada. 1979. Analytical Methods Manual. Water Quality Branch, Inland Waters Directorate, Ottawa.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics, and Chemistry. John Wiley & Sons, New York. 1015 pp.

NAQUADAT. 1985a. National Water Quality Data Bank. Dictionary of Parameter Codes. Data Systems Section, Water Quality Branch, Environment Canada, Ottawa.

NAQUADAT. 1985b. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reid, G.K. and R.D. Wood. 1976. Ecology of Inland Waters and Estuaries. D. Van Nostrand Co., Toronto, Ontario. 485 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

6.4.2 Dissolved Gas Supersaturation

Gases dissolve in water as a function of their partial pressures and solubilities. The solubility of a gas in water is limited and has a finite value. The amount of gas dissolved in water and the rate at which equilibrium is established will be determined by the nature of the gas, its partial pressure, ambient temperature and the presence of other solutes. Dissolved gas supersaturation occurs when the amount of gas dissolved in solution exceeds the amount anticipated at equilibrium. When supersaturation occurs, the diffusion pressure imbalance between the dissolved gas phase and the atmospheric phase favours a net transfer of gas to the atmospheric phase. Generally, this transfer cannot be accomplished fast enough by diffusion alone to prevent the formation of gas bubbles. Supersaturation can result in gas bubble disease, which has been observed in a wide variety of freshwater and marine fishes and invertebrates (U.S. EPA 1973; Harvey 1975; Weitkamp and Katz 1980). Gas bubble disease is defined as a noninfectious, physically induced process caused by uncompensated, hyperbaric total dissolved gas pressure, which produces primary lesions in blood and tissue and subsequent physiological dysfunction. Gas bubbles can form in aquatic organisms only when the sum of the dissolved gas pressures exceeds the sum of the hydrostatic and other compensatory pressures, such as blood pressure (Bouck 1980).

The primary modifying factors that affect gas solubility in water are pressure and temperature. According to Henry's law, the mass of a gas dissolved in a given volume of solvent, at a constant temperature, is proportional to the pressure of the gas with which it is in equilibrium. Hence, as the pressure of a given volume of solvent, in this case water, increases, the capacity of that volume of solvent to hold dissolved gases also increases. In water, hydrostatic pressure increases rapidly with depth, thus greatly increasing the capacity of deeper water to hold dissolved gases. The capacity of water to hold dissolved gas is inversely proportional to temperature. Hence, in water already saturated, increasing water temperature will produce supersaturation (Harvey 1975; Weitkamp and Katz 1980).

The gases of importance in gas bubble disease are nitrogen, oxygen and argon. According to Dalton's law of partial pressures, the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases. For dry air free of carbon dioxide and a total pressure of 101.3 kPa, the fractional composition of the principal gases is 78% nitrogen, 21% oxygen and 1% argon. Nitrogen and argon are normally considered together, as they are biologically inert towards fish, whereas oxygen is a biologically active gas. These gases will dissolve in water in relation to their solubilities and partial pressures. Although a principal component in gas bubble disease, nitrogen is not the sole gas of importance, and, hence, total dissolved gas pressure should be considered. Several studies have shown that the gas bubbles found in aquatic organisms suffering from gas bubble disease have compositions essentially identical to that of air (U.S. EPA 1973).

6.4.2.1 References

Bouck, G.R. 1980. Etiology of gas bubble disease. Trans. Am. Fish. Soc. 109: 703-707.

Harvey, H.H. 1975. Gas diseases in fish – a review. *In* Chemistry and Physics of Aqueous Gas Solutions. W.A. Adams, G. Greer, J.E. Desnoyers, G. Atkinson, G.S. Kell, K.B. Oldham and J. Walkley (eds.). The Electrical Society, Inc., Princeton, New Jersey. pp. 450-485.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033.

Weitkamp, D.E. and M. Katz. 1980. A review of dissolved gas supersaturation literature. Trans. Am. Fish. Soc. 109: 659-702.

6.4.3 Odour

6.4.3.1 Introduction

Odour perception (or olfaction) is one of the chemical senses. It is a complex sensation perceived by receptor organs in the nasal cavity. The sense of smell generally responds to a much lower concentration of a substance (parts per billion or less) than does the sense of taste (parts per million or more). Groundwater tends to have less of an odour than surface water (Health and Welfare Canada 1980).

Odour is rarely indicative of the presence of harmful substances in water, but may indicate a higher than desirable biological activity in a body of water used as a source of drinking water (Health and Welfare Canada 1980).

6.4.3.2 Sources

Odour from water seems to be the result of labile volatile organic compounds. Aquatic plants and various phytoplankton are a source of odour. Diatoms produce aromatic odours; for example, *Asterionella* sp. has a smell similar to a rose geranium, blue-green algae have a grassy odour, and some green and yellow algae have a fishy odour (Hutchinson 1957). Industrial wastes can create odours directly in water, or human activity can create conditions that stimulate odour-causing biological activity. For example, raw sewage stimulates biological growth and subsequent odours. Also, organic materials containing compounds such as tannins, lignins and humic substances, some inorganic chemicals and oil and gas impart odour to water. Water treatment can convert weak-smelling substances, such as phenols and amines, to substances with very strong odours, such as chlorophenols and chloramines (Health and Welfare Canada 1980).

6.4.3.3 Measurement

The threshold odour number (TON), defined as the greatest dilution of a sample with odour-free water to yield the least definitely perceptible odour, and the odour intensity index (OII), defined as the number of times the concentration of a water sample has to be halved by the addition of odour-free water to obtain the least definitely perceptible odour, are two commonly used measurements of the presence of odourants in water (ASTM 1976). Both have weaknesses that result in highly variable values from different judges. These tests are based on the concept that the higher the original concentration of an odourant, the more it can be diluted and still remain perceptible; underlying this concept is the incorrect assumption that all human judges perceive all odours in a constant manner. Because odour thresholds for different compounds vary for individuals, the test is actually measuring each judge's threshold levels of perception (and any particular anosmias) for different odourants. Other methods, such as rating the presence and intensity of odours relative to a standard vocabulary and associated reference standards, or the use of a trained flavour profile panel (which rates both odour and flavour), are more appropriate.

6.4.3.4 Factors Affecting Odour

Many factors affect the presence of odourants and the production of odour in water supplies, including stagnant conditions and flow rate, storm conditions causing high runoff and turbulence disturbing odour-producing substances. Temperature affects the vapour pressure of volatile substances, and hence odour intensity will be directly related to temperature. Warmer temperatures increase growth rate and the production of odour-causing metabolic and decay products. The production of such substances as chlorophenols is faster at higher water temperatures. The pH of the water can affect odour by controlling the equilibrium between odour-causing and odour-free forms of a substance; pH also affects the rate of some chemical reactions that lead to odour production (Health and Welfare Canada 1980).

Some toxic chemical groups can be detected by their odour at lower concentrations than those known to be toxic, and this odour characteristic is used when determining the water quality objective (Health and Welfare Canada 1980).

6.4.3.5 References

ASTM. 1976. Annual Book of ASTM Standards. Part 31. Water. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Health and Welfare Canada. 1980. Odour. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 23-32.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, New York. 1015 pp.

6.4.4 Specific Conductance (Conductivity)

Specific conductance (conductivity) is a numerical expression of water's ability to conduct an electrical current. The principal factors that influence the conductivity of an aqueous solution include the nature and concentration of the solutes present, the degree to which they dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution. Conductivity is usually expressed in microsiemens per centimetre ($\mu\text{S}\cdot\text{cm}^{-1}$). The conductivity of seawater is usually expressed in terms of salinity. Solutions of most inorganic acids, bases and salts are relatively good conductors. Alternatively, organic compounds that do not dissociate in aqueous solution conduct either no or very little current (McNeely *et al.* 1979; Greenberg *et al.* 1981; Hem 1982).

Table 6-162. Environmental Ranges of Specific Conductance in Canadian Surface Waters

Region	Range ($\mu\text{S}\cdot\text{cm}^{-1}$)	Number of samples	Sampling year(s)
Western	4.8[1]-84 600	6 321	1980-1985
	20[2]-13 500	19	Prior to 1980
Central	1[1]-2000	6 781	1980-1985
	0.003-500	206	1980-1985
Atlantic	0.008-31 000	11 424	1980-1985
	3.2[2]-740	1 003	1980-1985

[1] Detection limit is 0.2 $\mu\text{S}\cdot\text{cm}^{-1}$.

[2] Detection limit is 2.5 $\mu\text{S}\cdot\text{cm}^{-1}$.

Source: NAQUADAT 1985.

Conductivity is particularly sensitive to variations in dissolved solids; its measurement, however, provides no indication of the relative quantities of the various components comprising dissolved solids. For most natural waters, however, conductivity (in $\mu\text{S}\cdot\text{cm}^{-1}$) may be related to dissolved solids (in $\text{mg}\cdot\text{L}^{-1}$) by multiplying the conductance by a factor ranging from 0.55 to 0.75. This conversion may be tenuous, however, because the multiplication factor may be closer to 1.0 for water containing significant concentrations of sulphate, but less than 0.5 for acidic or basic solutions. The conversion should not be attempted if the dominant ion is unknown. Studies in the Susquehanna River basin in Pennsylvania and New York indicated that conductivity could be converted to concentration of dissolved solids by multiplying by a factor of 0.626, with a standard error in the reported concentration of dissolved solids of ±16.6 $\text{mg}\cdot\text{L}^{-1}$ (Lystrom *et al.* 1978).

Environmental ranges of specific conductance in Canadian surface waters are presented in Table 6-162.

Ten samples taken between 1980 and 1982 from a NAQUADAT station in British Columbia had specific conductance ranges of 3080-12 200 $\mu\text{S}\cdot\text{cm}^{-1}$. One NAQUADAT station sampled in 1983 in Newfoundland reported a specific conductance of 36 000 $\mu\text{S}\cdot\text{cm}^{-1}$ for municipal wastewater (detection limit 0.2 $\mu\text{S}\cdot\text{cm}^{-1}$). One NAQUADAT station in Newfoundland had a specific conductance range of 1920 to 3300 $\mu\text{S}\cdot\text{cm}^{-1}$ (detection limit 2.5 $\mu\text{S}\cdot\text{cm}^{-1}$) for municipal wastewater based on three samples taken in 1982 and 1983 (NAQUADAT 1985).

6.4.4.1 References

Greenberg, A.E., J.J. Connors and D. Jenkins (eds.). 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

Hem, J.D. 1982. Conductance: a collective measure of dissolved ions. *In* Water Analysis. Vol. I. Inorganic Substances. Part I. R.A.

Minear and L.H. Keith (eds.). Academic Press, New York. pp. 137-161.

Lystrom, D.J., F.A. Rinella and W.D. Knox. 1978. Definition of regional relationships between dissolved solids and specific conductance, Susquehanna River basin, Pennsylvania and New York. U.S. Geol. Surv. J. Res. 6: 541-545.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Specific conductance. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. p. 55.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

6.4.5 Taste

Taste is the sensation perceived by the receptors on the tongue. There are four basic tastes – sweet, salt, sour and bitter – which may be perceived alone or in combination. Flavour is a term usually equated solely with taste; however, it is more a function of odour perception as the sample is being placed in the mouth and moves from the back of the mouth through the connection to the nasal cavity, with the contribution of taste perception being secondary. Specific characteristics of a sample that are perceived as it is taken into the mouth may be described as "flavour notes", and are a combination of the two phenomena plus some aspects of texture, such as astringency and soapiness.

Taste may be measured by rating the presence of specific flavour notes relative to reference standards, or by a flavour profile panel (see Section 6.4.3).

The taste of water can be defined as the sensation that results from the presence of substances in water that have negligible vapour pressures and negligible odours. Nuances of taste are thought to be related to the degree to which various taste papillae respond to sensations of sweetness, sourness, saltiness and bitterness (Health and Welfare Canada 1980).

Taste can be derived from a number of factors, including industrial activity and biological origins. Taste from biological origins may fluctuate with season (Health and Welfare Canada 1980). Taste and odour incidents per year in Canada are in the range of 10 to 100, excluding persistent problems caused by iron or minerals (Brownlee 1986). Some of the factors affecting the taste of water are discussed below.

1. Temperature: An optimum taste response is obtained for water at or near body temperature. Chilling and heating (55°C) significantly reduce the taste intensity of water. It has been shown that the degree to which taste is influenced by temperature is a function of the specific taste-causing substance (Pangborn and Bertolero 1972). Temperature also affects the taste of water according to how it influences the chemical equilibrium of substances causing taste. Elevated temperatures enhance the production of bad-tasting metabolites of microorganisms and also accelerate the production of unpleasant-tasting corrosion products (Health and Welfare Canada 1980).
2. pH: The pH of water can directly influence taste by controlling the equilibrium concentration of neutral and ionized forms of a substance in solution. The pH of a solution also has a strong effect on reactions that produce products that have strong tastes, such as chlorophenols (Health and Welfare Canada 1980).
3. Microorganisms: A number of offensive tastes (and odours) are caused by microorganisms. An example of this is the taste caused by the release of relatively high iron concentrations in distribution systems by nuisance organisms called (nonspecifically) "iron bacteria" (Health and Welfare Canada 1980). Excessive algal growth in water bodies, used as a drinking water source, can produce organic compounds such as geosmin or 2-methylisorboneol which cause the taste/odour problems (Brownlee 1986).
4. Residual chlorine: Taste sensitivity to hypochlorous acid was greater than that to the hypochlorite ion, and the taste threshold concentration of free residual chlorine increased from 0.075 to 0.45 $mg{\cdot}L^{-1}$ as pH increased from 5.0 to 9.0 (Bryan *et al.* 1973). Other studies have suggested that the taste threshold is higher (>1.5 $mg{\cdot}L^{-1}$) (Health and Welfare Canada 1980).
5. Total dissolved solids: The major cations and anions play a large role in the taste of water. The taste threshold concentrations of many cations are much higher than the concentrations that are found in water, with the possible exceptions of magnesium and calcium. The thresholds for magnesium and calcium are approximately 100 and 125 $mg{\cdot}L^{-1}$, respectively (Lockhart *et al.* 1955). The taste effect of the major associated anions is often more intense than the metal ion tastes (Bruvold 1975), and thus the threshold for calcium and magnesium would not be reached before the water was rejected (Health and Welfare Canada 1980).
6. Iron and sulphide: These are well-known causes of taste impairment. The range of sensitivity to the taste of iron is very wide. Hydrogen sulphide predominates over bisulphide at the normal pH range of drinking water, and bisulphide predominates at pH 8.0. The sulphide ion becomes appreciable only above pH 10 (Health and Welfare Canada 1980).

Taste, as a quality of water, has very wide-ranging effects because of peoples' sensitivities and likes and dislikes. One danger in using water that has an unpleasant taste, but is otherwise suitable as a source of drinking water, would be its rejection by people, some of whom may select an unsafe source as a replacement (Health and Welfare Canada 1980).

6.4.5.1 References

Brownlee, B.G. 1986. Personal communication. National Water Research Institute, Environment Canada, Burlington, Ontario.

Bruvold, W.H. 1975. Human perception and evaluation of water quality. Crit. Rev. Environ. Control 5: 153-231. (Cited in Health and Welfare Canada 1980.)

Bryan, P.E., L.N. Kuzminski, F.M. Sawyer and T.H. Feng. 1973. Taste thresholds of halogens in water. J. Am. Water Works Assoc. 65: 363-368.

Health and Welfare Canada. 1980. Taste. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 51-63.

Lockhart, E.E., C.L. Tucker and M.C. Merritt. 1955. The effect of water impurities on the flavour of brewed coffee. Food Res. 20: 598-605. (Cited in Health and Welfare Canada 1980.)

Pangborn, R. and L. Bertolero. 1972. Influence of temperature on taste intensity and degree of liking of drinking water. J. Am. Water Works Assoc. 64: 511-515.

6.4.6 Temperature

6.4.6.1 Introduction

Temperature may be defined as the condition of a body that determines the transfer of heat to, or from, other bodies. It is normally measured with either a thermometer or thermistor, and is expressed on a relative scale such as the Celsius (°C) or Farenheit (°F) scales. Temperature variations are part of the normal climatic regime, and natural bodies of water exhibit seasonal and diurnal variations as well as vertical stratification. The temperature of surface waters is influenced by factors such as latitude, elevation, season, time of day, rate of flow and depth (McNeely *et al.* 1979).

Temperature plays a major controlling role in the aquatic environment; it conditions the influences of a variety of physical-chemical parameters. In general, as temperature increases from 0 to 30°C, viscosity, surface tension, compressibility, specific heat, ionization constant and latent heat of vaporization decrease, whereas thermal conductivity and vapour pressure increase. Gas (H_2, N_2, CO_2 and O_2) solubilities also decrease with increasing temperature (Houston 1982). Aquatic organisms have upper and lower thermal tolerance limits, optimum temperatures for growth, preferred temperature in thermal gradients and temperature limitations for migration, spawning and egg incubation (U.S. EPA 1973).

6.4.6.2 Sources of Temperature Change in the Aquatic Environment

The temperature of a water body is primarily a reflection of the climatic regime; anthropogenic activities can, however, alter the temperature of receiving waters (McNeely *et al.* 1979). In Canada, thermal discharges to receiving waters arise mainly from the operation of fossil- and nuclear-fuelled electricity-generating plants, from industries such as steel manufacturing and from sewage treatment plants. Electricity generated by thermal power accounts for approximately 75% of the total heat discharged to the Canadian aquatic environment (Dickson 1975). The release of cool hypolimnetic waters from impoundments may introduce cooler water into receiving waters (McNeely *et al.* 1979).

6.4.6.3 Environmental Range

The temperature of natural inland surface waters in temperate regions generally ranges from 0 to 30°C; maximal values occur particularly in shallow water in summer, whereas minimal values, occasionally falling below 0°C, occur in winter. Temperatures up to 40°C have been found in hot springs. Groundwater tends to exhibit lower and somewhat more uniform temperatures than do surface waters (McNeely *et al.* 1979).

Environmental ranges for temperature in Canadian surface waters are presented in Table 6-163.

Table 6-163. Environmental Ranges of Temperature in Canadian Surface Waters

Region	Range (°C)	Number of samples	Sampling year(s)
Pacific	−1[1]-40.5	2688	1980-1985
Central	4.1[2]-24.96	2738	1980-1985
	−1[1]-29.5	3871	1980-1985
Quebec	10.3[3]-17.4	7	1981-1982
Atlantic	0[3]-30.3	982	1980-1985

[1] Water temperature measured in Hg-filled thermometer.

[2] Temperature of deepest water where sampling took place.

[3] Water temperature measured is accurate to 0.5°C.

Source: NAQUADAT 1985.

6.4.6.4 References

Dickson, D.R. 1975. Waste Heat in the Aquatic Environment. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 14109. 39 pp.

Houston, A.H. 1982. Thermal Effects Upon Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18566. 200 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Temperature. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 59-60.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033. 594 pp.

6.4.7 Total Dissolved Solids

6.4.7.1 Introduction

The measurement of total dissolved solids (TDS) is an index of the amount of dissolved substances in water, and gives a general indication of the chemical quality. TDS is defined analytically either by total filterable residue ($mg \cdot L^{-1}$) or by conductivity ($\mu S \cdot cm^{-1}$) (Faust and Aly 1981). The component elements covered by the term total dissolved solids are essential constituents of living matter.

6.4.7.2 Sources and Pathways for Entering the Aquatic Environment

The concentration of total dissolved solids in water depends on the weathering characteristics of igneous and sedimentary rocks, runoff from soils and the influence of anthropogenic sources. The latter can be municipal and industrial effluents, agricultural runoff and atmospheric deposition (Faust and Aly 1981). One NAQUADAT station sampled in 1980 and 1982 in British Columbia reported a TDS concentration range of 424-3300 $mg \cdot L^{-1}$ (detection limit 2 $mg \cdot L^{-1}$) for nine samples taken from industrial wastewater (NAQUADAT 1985).

The TDS content of open lake waters, where water is drained by streams or rivers, reflects the inorganic composition of influent water. The TDS concentration of lakes that are not drained, or that lack a significant effluent discharge (closed lakes), is modified by precipitation and the concentration of solutes (such as salts) by evaporation. Fluvial waters are much more varied in TDS content than is standing water, but larger streams, especially major rivers, are generally similar in inorganic composition to open lakes (Reid and Wood 1976).

6.4.7.3 Environmental Concentrations

Concentrations of total dissolved solids are lowest in regions of bare igneous rock, and the water is referred to as "soft". Highest concentrations are in regions with calcareous sediments from which soluble salts can be leached; such water containing high concentrations of salts is called "hard" (Reid and Wood 1976).

The concentrations of total dissolved solids vary widely, from very low (<10 mg·L^{-1}) to thousands of milligrams per litre in saline lakes. Most lakes occupying open basins have TDS concentrations of 100-200 mg·L^{-1} (Reid and Wood 1976). The Western region was the only region to report total dissolved solids concentrations in NAQUADAT. The concentrations ranged from 4 to 65 879 mg·L^{-1}, based on 2223 samples taken between 1980 and 1985 (NAQUADAT 1985).

Environmental concentration ranges for filterable residues in Canadian surface waters are presented in Table 6-164. The relationship between TDS and salinity is given in Table 6-165.

6.4.7.4 Forms and Fate in the Aquatic Environment

Dissolved solids or total dissolved solids (TDS) are terms generally associated with the amount of inorganic salts, organic matter and dissolved materials that are present in fresh water (Sawyer 1960). In general, TDS usually refers to the inorganic substances that are dissolved in water. The principal inorganic anions that are dissolved in water include carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates. The principal cations are calcium, magnesium, sodium, potassium, nitrogen, phosphorus, iron, sulphur and silicon. A few other elements occur in small amounts (Reid and Wood 1976).

The measurement of filterable residues is often considered to be equivalent to that of TDS (Greenberg *et al.* 1981; Hem 1982). The term salinity, although not precisely equivalent to total dissolved salt content, is usually considered to be related to it, and is generally defined as the total concentration of ionic components (Hutchinson 1957; Reid and Wood 1976). Salinity has been operationally defined as the total solid content of water after all carbonates have been oxidized, all bromide and iodide replaced by chloride and all organic matter oxidized. It is usually numerically smaller than the filterable residue (Greenberg *et al.* 1981).

The measurement of specific conductance may provide an indication of the amount of TDS present in water. The relationship between specific conductance and TDS will vary depending upon the distribution of the major cations and anions present in a particular water sample. Conductance measurements, however, do not account for uncharged molecular species such as silicic acid ($Si(OH)_4$), which is expected to occur in TDS residues in the form of silicon dioxide (SiO_2). Furthermore, volatile solutes are not measured in standard TDS or filterable residue determinations (Hem 1982). TDS may also be determined by summing all the measured concentrations of dissolved or filterable substances in a sample (Health and Welfare Canada 1980).

Table 6-164. Environmental Concentration Ranges for Filterable Residues in Canadian Surface Waters

Region	Concentration range (mg·L^{-1})	Number of samples	Sampling year(s)
Pacific	ND[1,2]-990	972	1980-1985
Western	0.002-5873	1784	Prior to 1980
Central	0.2-23 536	2394	Prior to 1980
Atlantic	1[1]-3284	1087	1980-1985

[1] Detection limit is 2 mg·L^{-1}.

[2] ND = not detected.

Source: NAQUADAT 1985.

Table 6-165. Total Dissolved Solids – Salinity Relationship

Concentration range of total dissolved solids (mg·L^{-1})	Degree of salinity
0-1 000	Fresh; nonsaline
1 001-3 000	Slightly saline – brackish
3 001-10 000	Moderately saline – brackish
10 001-100 000	Saline
>100 000	Brine

Source: McNeely *et al.* 1979.

6.4.7.5 References

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 400 pp.

Greenberg, A.E., J.J. Connors and D. Jenkins (eds.). 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

Health and Welfare Canada. 1980. Total dissolved solids. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 603-612.

Hem, J.D. 1982. Conductance: a collective measure of dissolved ions. *In* Water Analysis. Vol. I. Inorganic Species. Part 1. R.A. Minear and L.H. Keith (eds.). Academic Press, New York. pp. 137-161.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. 1. Geography, Physics and Chemistry. John Wiley & Sons, Inc., New York. 1015 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Total dissolved solids. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 61-62.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Reid, G.K. and R.D. Wood. 1976. Ecology of Inland Waters and Estuaries. D. Van Nostrand Co., New York. 485 pp.

Sawyer, C.N. 1960. Chemistry for Sanitary Engineers. McGraw-Hill Book Co., New York.

6.4.8 Turbidity, Clarity and Suspended Solids

6.4.8.1 Introduction

Turbidity in water is caused by the presence of suspended matter such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, plankton and other microscopic organisms that are held in suspension by turbulent flow and Brownian movement (McNeely *et al.* 1979). Turbidity is an expression of the optical property of water that causes incident light to be scattered and absorbed rather than transmitted in straight lines through the sample (Vanous *et al.* 1982). The correlation between turbidity and the weight concentration of suspended and settleable solids is often tenuous, however, because the shape, size, refractive index and chemical composition of the particulates in aqueous systems may affect the light-scattering properties (Vanous *et al.* 1982).

Water clarity is important in water for human consumption and also in numerous industries producing materials destined for human consumption, such as the food and beverage industry and various manufacturing industries (Greenberg *et al.* 1981). The clarity of water is often measured using a Secchi disc. The point (depth of water) of the disc's disappearance and reappearance when suspended in water gives an indication of the limit of visibility in water. As it is a simple method, the Secchi disc is often used to estimate visibility at bathing beaches (Greenberg *et al.* 1981).

Suspended solids are measured in milligrams per litre, and correspond to the solids that are retained in a filter. They are part of the total residue that is left in the containers after evaporation of a sample and its subsequent drying in an oven. Total residue (or total solids) includes nonfilterable (dissolved) and filterable (suspended) solids, and should not be confused with total suspended solids (Greenberg *et al.* 1981).

6.4.8.2 Sources and Pathways for Entering the Aquatic Environment

The major part of suspended material found in most natural waters is made up of soil particles derived from land surfaces by erosion. Microscopic algae and zooplankton contribute to turbidity in natural waters; their density varies according to season (McNeely *et al.* 1979). Asbestos, a group of naturally occurring hydrate silicate minerals possessing a fibrous morphology, is an identified component of suspended material in drinking water sources (Health and Welfare Canada 1980). The particles that cause turbidity in water range in size from colloidal dimensions (approximately 10 nm) to diameters in the order of 0.1 mm. In general, during a yearly cycle, turbidity is highest during spring runoff (McNeely *et al.* 1979).

6.4.8.3 Environmental Range

Raw water levels of turbidity can range from 1 to 1000 NTU (Nephelometric Turbidity Units), and can change quickly during periods of surface runoff, for example, during the first hour of a rainfall occurrence (U.S. EPA 1978). The second unit used in measurement, JTU (Jackson Turbidity Units), is not practical below 25 units because of limits of the measuring device, but it has the advantage of long history of use (Thurston *et al.* 1979).

Four groundwater wells in Newfoundland were sampled for turbidity and suspended solids. The concentration range was 270-15 000 JTU based on four samples taken in 1981. Municipal treated water (Quebec) was sampled for turbidity and suspended solids. One station had a concentration of 90 and 94 JTU based on two samples taken in 1984. Ten other Quebec stations reported a concentration range of 20-37 NTU for 10 samples taken in 1984 (NAQUADAT 1985).

Table 6-166. Environmental Ranges for Turbidity and Suspended Solids in Canadian Surface Waters

Region	Range (JTU or NTU)	Number of samples	Sampling year(s)
Pacific	0.12[1]-360	1449	1980-1985
Western	0.1[1]-3600	5809	1980-1985
Central	ND[1,2]-90	2205	1980-1985
Atlantic	ND[1]-520	9848	1980-1985
	0.22[3]-3.1	108	Prior to 1980

[1] JTU (Jackson Turbidity Units).

[2] ND = not detected.

[3] NTU (Nephelometric Turbidity Units).

Source: NAQUADAT 1985.

Environmental ranges for turbidity and suspended solids in Canadian surface waters are presented in Table 6-166.

6.4.8.4 References

Greenberg, A.E., J.J. Connors and D. Jenkins (eds.). 1981. Standard Methods for the Examination of Water and Wastewater. 15th edition. American Public Health Association, Washington, D.C. 1134 pp.

Health and Welfare Canada. 1980. Turbidity. *In* Guidelines for Canadian Drinking Water Quality 1978. Supporting Documentation. Supply and Services Canada, Ottawa. pp. 77-96.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Turbidity. *In* Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. pp. 62-63.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Thurston, R.V., R.C. Russo, C.M. Fetterolf, Jr., T.A. Edsall and Y.M. Barber, Jr. (eds.). 1979. Solids (suspended, settleable) and turbidity. *In* A Review of the EPA Red Book: Quality Criteria for Water. Water Quality Section, American Fisheries Society, Bethesda, Maryland.

U.S. EPA. 1978. Urban Stormwater Management Work Shop Proceedings. Dec. 1, 1977. Edison, New Jersey. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency. EPA-600/9-78-017. 110 pp.

Vanous, R.D., P.E. Larson and C.C. Hach. 1982. The theory and measurement of turbidity and residue. *In* Water Analysis. Vol. I. Inorganic Species. Part 1. R.A. Minear and L.H. Keith (eds.). Academic Press, New York. pp. 163-234.

6.5 RADIOLOGICAL PARAMETERS

6.5.1 Uses and Sources for Entry Into the Aquatic Environment

The presence of radionuclides in the aquatic environment arises from natural sources and man's activities (Whicker and Schultz 1982). Natural sources of radionuclides are the interaction of cosmic rays with atmospheric nuclides and the weathering of rocks containing radioactive elements, such as uranium and thorium and their daughter products. Human activities, such as testing of nuclear weapons in the atmosphere and nuclear fuel cycle operations, e.g. uranium mining and milling, nuclear power generation, and industrial/

medical uses of radioisotopes, can add significant quantities of radionuclides to the aquatic environment.

The proportion of natural versus man-made sources of radionuclides in the aquatic environment is usually variable. Prior to World War II, all the radiation in the environment was solely the result of natural processes. After the war, the testing of nuclear devices in the atmosphere resulted in the addition of significant quantities of fission and activation products to the aquatic environment until 1963, when a Limited Nuclear Test Ban Treaty was signed by the superpowers. Since 1963, the amount of radionuclides in the environment has decreased significantly.

Elevated concentrations of naturally occurring radionuclides can occur in fresh waters because of rich uranium/thorium deposits near the surface (B.C. Royal Commission 1980); uranium concentrations approaching or exceeding 10 $\mu g \cdot L^{-1}$ have been recorded in uranium mineralization areas of Summerland and Nelson in British Columbia. Activities of naturally occurring radionuclides may also be increased because of human activities. For example, uranium mining and milling in the Elliot Lake district of Ontario have increased the levels of ^{226}Ra, a daughter product of ^{238}U, in the Serpent River water system (Hart and McKee 1985).

Radionuclides have been used for the benefit of mankind in several ways. Uranium-235 is an isotope (0.72%) of natural uranium; this radionuclide is fissile and has been used to produce electricity. At present, approximately one-third of the electricity generated in Ontario comes from nuclear power generation. In addition, radioactive substances have been used in medicine, research and industry. In nuclear medicine, radioisotopes are used to determine the condition and operation of certain body organs. Also, radioisotopes have been used extensively in research as tracers. In industry, radiation is used to sterilize medical supplies and foods, and has many other industrial uses.

6.5.2 Pathways for Entering the Aquatic Environment

Aquatic ecosystems may receive radionuclides from point sources, such as nuclear fuel cycle operations, and from nonpoint sources, such as weathering of minerals and rocks containing radioactive substances. Radionuclides from these sources may enter the aquatic environment directly, or indirectly, via air, soil or sediments.

Radionuclides present in air may end up in water by precipitation scavenging and gravitational settling. Precipitation scavenging, by which most airborne radioactive materials are deposited, plays an important role for particles smaller than 10 μm in diameter (Menzel *et al.* 1963), whereas deposition from gravitational settling increases as the particles exceed 20 μm in diameter (Whicker and Schultz 1982).

Radionuclides present in soils and sediments can also reach large water bodies. Plants growing on soils take up radionuclides through their root systems. The plants may be consumed by humans or by herbivores which may then be eaten by humans. In addition, when the plants die they leave substantial portions of organic residues above ground. Water erosion and leaching will bring radionuclides to the aquatic environment.

6.5.3 Environmental Concentrations

For a radionuclide to be environmentally significant, it must be present at high enough concentrations in the aqueous media. In addition, the length of its half-life should be such that the radionuclide has high enough specific activity to present a potential radiological hazard. Consequently, a half-life greater than a few years and less than a million years will usually constitute a radiation hazard.

The average concentration of uranium in the earth's crust is about 1 $\mu g \cdot g^{-1}$ whereas that of thorium is somewhat higher (B.C. Royal Commission 1980; Cothern and Lappenbusch 1983; Hess *et al.* 1985). Thorium is relatively insoluble in most surface waters; hence, natural uranium and the daughter products of ^{238}U, which constitutes 99.3% of natural uranium, are of environmental concern. From human activities, radionuclides deposited from nuclear fallout and those released from nuclear power generation are generally believed to be of concern. Specifically, environmentally significant radionuclides from natural sources are total uranium and ^{226}Ra, whereas those from man-made sources are ^{137}Cs and ^{90}Sr. Tritium and ^{131}I are primarily released from nuclear power generation, and may be only locally important.

Most radionuclides have low solubilities and are readily sorbed onto the surfaces of solid particles; hence, the levels of radioactivity in natural waters are usually low. Also, surface waters generally have lower concentrations of radionuclides than do groundwaters.

The National Radionuclides Monitoring Program was initiated in 1981 by the Water Quality Branch of Environment Canada to assess the radiological status of selected surface waters across Canada; average concentrations of radionuclides are presented in Table 6-167. As is apparent from this table, the concentrations of radionuclides originating from natural sources (total uranium and ^{226}Ra) are somewhat higher than those from man-made sources. The mean concentration of total uranium is 1.35 $\mu g \cdot L^{-1}$, which is very close to the value of 1.5 $\mu g \cdot L^{-1}$ reported for U.S. waters by Cothern and Lappenbusch (1983). The average ^{226}Ra concentration is 3.66 $mBq \cdot L^{-1}$; this concentration is the same as that reported to be the upper concentration for surface waters, 3.7 $mBq \cdot L^{-1}$, by the B.C. Royal Commission (1980).

In contrast, the International Joint Commission concentrated its efforts on the measurement of man-made radionuclides in the Great Lakes; the data of Durham and Joshi (1984) for ^{137}Cs and ^{90}Sr are shown in Table 6-168. These data are in the same range as those reported by Meyerhof (1984) for the Ottawa River in recent years.

6.5.4 Forms and Fate in the Aquatic Environment

Once radionuclides have reached large water bodies, such as a river, they are subjected to dispersal processes; this results in reduction in the concentration of the radionuclides in the water, primarily as a result of dilution.

In water, the soluble portion of the radionuclides is usually reduced by precipitation, adsorption/ion exchange by the sediments and eventual uptake by biota (Joshi 1984), particularly fish. Hence, depending upon the chemical and physical

Table 6-167. Average Radionuclide Concentrations in Canadian Surface Waters between 1981 and 1984

Sampling location	Average radionuclide concentration[1]				
	^{226}Ra (mBq·L^{-1})	^{137}Cs (mBq·L^{-1})	^{125}Sb (mBq·L^{-1})	Tritium (Bq·L^{-1})	Total U (μg·L^{-1})
Ranger Bight, Lab.	4.44 ± 1.11	<13.69	<7.78	5.95 ± 2.34	0.70 ± 0.08
Annapolis River, N.S.	1.48 ± 0.30	<3.97	<8.98	6.02 ± 1.49	0.43 ± 0.05
McAskill Brook, N.S.	1.48 ± 0.60	<6.66	15.56 ± 9.45	4.70 ± 1.15	0.30 ± 0.04
Moose Creek, N.B.	1.66 ± 0.64	<3.39	<8.88	6.81 ± 1.78	1.37 ± 0.26
Petitcodiac River, N.B.	12.67 ± 10.14	<4.44	<7.17	7.88 ± 1.73	2.24 ± 1.91
Niagara River at Niagara-on-the-Lake, Ont.	2.19 ± 0.86	0.70 ± 0.32	<1.81	8.00 ± 0.88	0.48 ± 0.08
Niagara River at Fort Erie, Ont.	1.66 ± 0.26	<1.00	1.05 ± 0.40	5.12 ± 2.06	0.28 ± 0.17
St. Lawrence River at Wolfe Island, Ont.	1.43 ± 0.53	1.52 ± 0.33	<2.40	8.56 ± 1.67	0.57 ± 0.27
Souris River near Coulter, Man.	2.13 ± 1.22	<4.46	<6.93	7.64 ± 5.46	2.39 ± 1.14
Red River, Man.	3.88 ± 3.92	5.50 ± 4.33	<7.52	<6.33	4.74 ± 3.05
Sask. River at Man.-Sask. boundary	5.92 ± 1.70	<4.63	<8.35	<9.92	0.99 ± 0.07
Poplar River East, Sask.	7.03 ± 0.37	<3.50	<7.24	<6.48	2.84 ± 0.76
Baker Lake, N.W.T.	1.57 ± 0.70	4.22 ± 1.77	<10.19	12.24 ± 4.68	0.16 ± 0.08
Mean	3.66	–	–	–	1.35

[1] The values reported for each radionuclide are the means of the available data with their standard deviations.

Source: Baweja *et al.* 1986.

Table 6-168. Average Radionuclide Concentrations in the Great Lakes between 1973 and 1981

Great Lake	Average radionuclide concentration (mBq·L^{-1})	
	^{137}Cs	^{90}Sr
Lake Ontario	0.96	37.8
Lake Erie	0.68	28.3
Lake Huron	1.35	29.4
Lake Michigan	1.50	25.4
Lake Superior	2.10	16.6

Source: Durham and Joshi 1984.

characteristics of the medium, the proportion of radionuclides present in the water phase may be quite variable.

Cesium is strongly adsorbed by the sediments, especially clay mineral particles (Francis and Brinkley 1976). Inputs of ^{137}Cs and ^{90}Sr from atmospheric sources are generally equal. However, the concentrations found in water are quite variable. Because of stronger adsorption of cesium by sediments, Meyerhof (1984) found the concentration of ^{90}Sr in the Ottawa River to be severalfold higher than that of ^{137}Cs. Similarly, Baweja *et al.* (1986) found the concentration of ^{238}U in surface waters across Canada to be severalfold higher than that of ^{226}Ra, which is strongly adsorbed by the solid particulates.

6.5.5 References

Baweja, A.S., S.R. Joshi and A. Demayo. 1986. Radionuclide Content of Some Canadian Surface Waters: A Report on the National Radionuclides Monitoring Program – 1981 to 1984. Scientific Series, Inland Waters Directorate, Environment Canada, Ottawa. (In press.)

B.C. Royal Commission. 1980. Royal Commission of Inquiry into Uranium Mining. Commissioner's Report. Vol. 1. Queen's Printer for British Columbia, Victoria, British Columbia.

Cothern, R.C. and W.L. Lappenbusch. 1983. Occurrence of uranium in drinking water in the U.S. Health Phys. 45: 89-99.

Durham, R.W. and S.R. Joshi. 1984. Dose equivalent commitments from fallout radionuclides in the open waters of the Great Lakes, 1973-1981. Environ. Monit. Assess. 4: 405-417.

Francis, C.W. and F.S. Brinkley. 1976. Preferential adsorption of ^{137}Cs to micaceous minerals in contaminated freshwater sediments. Nature (London) 260: 511-513.

Hart, D.R. and P.M. McKee. 1985. Study to Assess the Distribution of Radionuclides in the Aquatic Ecosystem in the Vicinity of the Serpent River Mouth. Report prepared for Environment Canada on behalf of Beak Consultants Ltd., Mississauga, Ontario.

Hess, C.T., J. Michel, T.R. Horton, H.M. Prichard and W.A. Coniglio. 1985. The occurrence of radioactivity in public water supplies in the United States. Health Phys. 48: 553-586.

Joshi, S.R. 1984. ^{137}Cs, ^{226}Ra and total U in fish from Lakes Ontario, Erie, Huron, and Superior during 1976-1982. Water Pollut. Res. J. Can. 19: 110-119.

Menzel, R.G., H. Roberts, Jr., E.H. Stewart and A.J. Mackenzie. 1963. Strontium-90 accumulation on plant foliage during rainfall. Science 142: 576-577.

Meyerhof, D.P. 1984. Revisions to the Guidelines for Canadian Drinking Water Quality Radiological Characteristics. Paper presented at the 5th Annual Conference of the Canadian Radiation Protection Association, Banff, Alberta.

Whicker, E.W. and V. Schultz. 1982. Radioecology: Nuclear Energy and the Environment. Vol. I. Chap. 4. CRC Press, Inc., Boca Raton, Florida. pp. 73-128.

6.6 BIOLOGICAL PARAMETERS

6.6.1 Toxic Algae

6.6.1.1 Introduction

Toxic algae are found in all aquatic environments, and have been responsible for the death or illness of livestock, wildfowl, fish and humans (Carmichael 1981).

Well-known instances of marine algal toxicity are associated with "red tides", which cause fish kills and poison edible shellfish and other bottom fauna (Tangen 1977; Cross and Southgate 1980). On the west coast of North America, clams and mussels become poisonous by ingesting the dinoflagellate, *Gonyaulax catenella*, and accumulating the associated toxin, saxitoxin, in the digestive tract. On the east coast, the associated poisoning is caused by *G. tamarensis*, with a mixture of saxitoxin and three related toxins (Health and Welfare Canada 1983).

6.6.1.2 Toxic Species and Toxins

The most important taxonomic phyla containing toxic algae are Pyrrhophyta (dinoflagellates), Chrysophyta (phytoflagellates) and Cyanophyta (blue-green algae). The algae of most concern in lakes and ponds are usually blue-green algae which form massive "blooms" under certain conditions during summer (Reynolds and Walsby 1975; Carmichael *et al.* 1985). Lake water containing dense blooms of blue-green algae has the appearance and consistency of green pea soup.

The three blue-green algae most often identified as the cause of poisoning are *Anabaena flos-aquae*, *Aphanizomenon flos-aquae* and *Microcystis aeruginosa* (McLeod and Bondar 1952; Senior 1960; Aziz 1974; Moore 1977).

Most algal poisonings in western Canada are associated with blooms of *Anabaena flos-aquae*. Both toxic and nontoxic unialgal colony isolates of *An. flos-aquae* have been isolated from cows that had recently died after drinking water containing an algal bloom of this species.

The toxins produced by blue-green algae have been identified. There are thought to be at least four toxins associated with *An. flos-aquae*: anatoxins-*a*, -*b*, -*c* and -*d* (Carmichael and Gorham 1978). Anatoxin-*a*, an alkaloid, has a molecular weight of 165 (Figure 6-40) (Devlin *et al.* 1977). Its structure has been confirmed by X-ray crystallography (Huber) and synthesis (Devlin *et al.* 1977; Campbell *et al.* 1977).

Anatoxin-*a* causes death by respiratory arrest. The other anatoxins, -*b*, -*c* and -*d*, have not been identified in detail (Carmichael and Gorham 1978); they cause other symptoms as well, such as lacrimation and salivation, but the survival times are different.

Blooms of *Ap. flos-aquae* (blue-green) have caused the death of cattle. The toxin it produces has been shown to be a mixture of saxitoxin (Figure 6-41) (Schantz *et al.* 1975) and three related toxic compounds of unknown structure (Schimizu 1977). Saxitoxin is also known as paralytic shellfish poison, and received its name from the Alaskan butter clam *Saxidomus giganteus* (Schuett and Rapoport 1962).

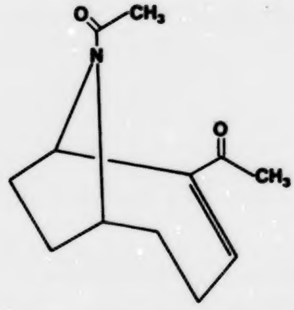


Figure 6-40. Anatoxin-a: 2-acetyl-9-azabicyclo[4.2.1]non-2-ene.

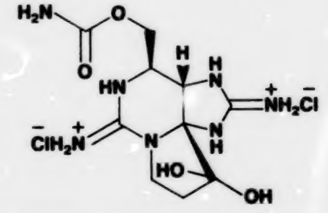


Figure 6-41. Saxitoxin dihydrochloride: 8-methyl-2-oxo-2,4,5,6-tetrahydropyrrolo[1,2-c]pyrimidine.

Microcystis toxins affect the central nervous system and the liver. Death occurs in 1-3 h. The toxins are small-molecular-weight polypeptides composed of 14 (Murthy and Capindale 1970) or 16 amino acids (Kirpenko *et al.* 1975). One study proposed that the polypeptide was cyclic, as it is unaffected by most proteolytic enzymes (Gorham 1962). A diarrhea toxin has been isolated from *M. aeruginosa*, and this may be a cause of gastroenteritis when no other known etiological agent can be identified (Aziz 1974). A number of other toxins have been recognized; some are lipid-soluble and some are water-soluble (Carmichael *et al.* 1985).

6.6.1.3 Occurrence in Fresh Waters

Outbreaks of blue-green algae (*An. flos-aquae*) have caused losses of wildfowl and wildlife (Rose 1953), and there are many examples of poisonings of cattle and dogs drinking from ponds and lakes during hot weather when dense blooms of floating blue-green algae have been blown into thick shoreline scums by the wind (Ingram and Prescott 1954). Animal deaths have been widely reported and reviewed in the United States (Ingram and Prescott 1954); there are also many examples of poisoning in Canada (O'Donoghue and Wilton 1951; McLeod and Bondar 1952; Neil 1957; Senior 1960; Carmichael and Gorham 1978). Death in livestock was recorded 1-2 h after ingestion of algae, with persistent vomiting occurring 15-30 min after drinking. Other symptoms include diarrhea and hemorrhagic enteritis. No other pathogens or toxic chemicals were found postmortem (Senior 1960).

There have been few recorded instances of illness in humans from swimming in lakes with blooms of toxic algae, but this may be more common than is thought because of lack of diagnosis. There is increasing evidence that the toxins cause gastroenteritis and contact irritation (Billings 1981). Lipopolysaccharide endotoxin is produced by some cyanophytes, and has been implicated in certain water-based outbreaks of gastroenteritis (Sykora and Keleti 1981). Toxic cyanophytes are becoming more of a concern, especially as more marginal water supplies are used by the public. There are reports indicating that toxins ingested from municipal drinking water supplies can cause illness (Lippy and Erb 1976; Keleti *et al.* 1979).

Fish kills (Prescott 1948) and the deaths of invertebrates because of blue-green algae have been reported by a number of authors. Inhibition and death of zooplankton caused by toxic cyanophytes have been demonstrated (Ransom *et al.* 1978; Snell 1980).

If not toxic directly, massive blooms of freshwater algae often cause die-offs of fish and other organisms when the algal population suddenly collapses. The death and rapid decomposition of the algae quickly lead to anoxia and asphyxiation of fish and other aquatic animals (Barica 1975; Nicholls *et al.* 1980).

6.6.1.4 Occurrence in Brackish and Estuarine Waters

In brackish water fish ponds in Israel and in estuarine areas in England, *Prymnesium parvum* (Prymnesiophyceae) produces a potent ichthyotoxin that is periodically responsible for the deaths of thousands of fish (Shilo 1971; Holdway *et al.* 1978). *Prymnesium parvum* is not known to cause similar problems in North America (Health and Welfare Canada 1983).

6.6.1.5 Occurrence in Marine Waters

Paralytic shellfish poisoning (PSP) has been recognized for more than a century. Filter feeders, such as bivalve molluscs and crustaceans, strain the toxic algae from the water. Mussels become too toxic for human consumption when algal densities in the water reach 100-200 cells per millilitre (Schantz *et al.* 1966). Two species of Pyrrhophyta have been identified as causative agents for PSP: *Gonyaulax catenella* on the west coast and *G. tamarensis* along the shores of Quebec and New Brunswick (Needler 1949). The toxins are retained by different organs in the toxin-concentrating shellfish. In *Mytilus* sp. (mussel), the toxins are chiefly found in the hepatopancreas, and in *Mya arenaria* (soft shell clam) and *Spisula sollidissima* (bar clam), the toxins are found in the gills (Prakash *et al.* 1971).

Shellfish that feed on toxic as well as nontoxic algae show no distinguishing signs in their appearance when feeding on toxic algae. A mechanism exists in the shellfish which binds the toxin in the dark gland or the syphon. After the toxic algae have disappeared from the water, the shellfish can excrete or destroy the toxins in a couple of weeks. This is not the case with the Alaska butter clam, as about 60-80% of the saxitoxin is bound to the siphon. It takes about 12 months, because of low metabolic activity, to clear the toxin from the clam (Schantz 1981).

6.6.1.6 References

Aziz, K.M.S. 1974. Diarrhea toxin obtained from a waterbloom-producing species, *Microcystis aeruginosa* Kützing. Science 183: 1206-1207.

Barica, J. 1975. Collapses of algal blooms in prairie pothole lakes: their mechanism and ecological impact. Verh. Int. Ver. Theor. Angew. Limnol. 19: 606-615.

Billings, W.H. 1981. Water associated human illness in northeast Pennsylvania and its suspected association with blue-green algae blooms. *In* The Water Environment: Algal Toxins and Health. W.W. Carmichael (ed.). Plenum Press, New York. pp. 243-255.

Campbell, H.F., O.E. Edwards and R. Kolt. 1977. Synthesis of noranatoxin-A and anatoxin-A. Can. J. Chem. 55: 1372-1379. (Cited in Moore 1977.)

Carmichael, W.W. 1981. Freshwater blue-green algae (Cyanobacteria) toxins – A review. *In* The Water Environment: Algal Toxins and Health. W.W. Carmichael (ed.). Plenum Press, New York. pp. 1-13.

Carmichael, W. and P.R. Gorham. 1978. Anatoxins from clones of *Anabaena flos-aquae* isolated from lakes of western Canada. Mitt. Int. Ver. Theor. Angew. Limnol. 21: 285-295.

Carmichael, W.W., C.L.A. Jones, N.A. Mahmood and W.C. Theiss. 1985. Algal toxins and water-based diseases. CRC Crit. Rev. Environ. Control 15: 275-313.

Cross, T.F. and T. Southgate. 1980. Mortalities of fauna of rocky substrates in south-west Ireland associated with the occurrence of *Gyrodinium aureolum* blooms during autumn 1979. J. Mar. Biol. Assoc. U.K. 60: 1071-1073.

Devlin, J.P., O.E. Edwards, P.R. Gorham, N.R. Hunter, R.K. Pike and B. Stavric. 1977. Anatoxin-A, a toxic alkaloid from *Anabaena flos-aquae* NRC-44h. Can. J. Chem. 55: 1367-1371. (Cited in Moore 1977.)

Gorham, P.R. 1962. Laboratory studies on the toxins produced by waterblooms of blue-green algae. Am. J. Public Health 52: 2100-2105. (Cited in Moore 1977.)

Health and Welfare Canada. 1983. Guidelines for Canadian Recreational Water Quality. Supply and Services Canada, Ottawa.

Holdway, P.A., R.A. Watson and B. Moss. 1978. Aspects of the ecology of *Prymnesium parvum* (Haptophyta) and water chemistry in the Norfolk Broads, England. Freshwater Biol. 8: 295-311.

Ingram, W.M. and G.W. Prescott. 1954. Toxic fresh-water algae. Am. Midl. Nat. 52: 75-87.

Keleti, G., J.L. Sykora, E.C. Lippy and M.A. Shapiro. 1979. Composition and biological properties of lipopolysaccharides isolated from *Schizothrix calcicola* (Ag.) Gomont (Cyanobacteria). Appl. Environ. Microbiol. 38: 471-477. (Cited in Carmichael 1981.)

Kirpenko, Yu.A., I.I. Perevozchenko, K.A. Sirenko and L.F. Lukina. 1975. Isolation of toxin from blue-green algae biomass and some of its physicochemical properties. (Transl. from Russian.) Dopov. Akad. Nauk Ukr. RSR Ser. B 37: 359-361. (Cited in Moore 1977.)

Lippy, E.C. and J. Erb. 1976. Gastrointestinal illness at Sewickley, Pa. J. Am. Water Works Assoc. 68: 606-610. (Cited in Carmichael 1981.)

McLeod, J.A. and G.S. Bondar. 1952. A case of suspected algal poisoning in Manitoba. Can. J. Public Health 43: 347-350.

Moore, R.E. 1977. Toxins from blue-green algae. BioScience 27: 797-802.

Murthy, R.J. and J.B. Capindale. 1970. A new isolation and structure for the endotoxin from *Microcystis aeruginosa* NRC-1. Can. J. Biochem. 48: 508-510.

Needler, A.B. 1949. Paralytic shellfish poisoning and *Gonyaulax tamarensis*. J. Fish. Res. Board Can. 7: 490-504.

Neil, J.H. 1957. Problems and control of unnatural fertilization of lake waters. *In* Proc. 12th Ind. Waste Conf. May, Purdue Univ., Lafayette, Indiana. pp. 301-316.

Nicholls, K.H., W. Kennedy and C. Hammett. 1980. A fish-kill in Heart Lake, Ontario, associated with the collapse of a massive population of *Ceratium hirundinella* (Dinophyceae). Freshwater Biol. 10: 553-561.

O'Donoghue, J.G. and J.G.S. Wilton. 1951. Algae poisoning in Alberta. Can. J. Comp. Med. 15: 193-198.

Prakash, A.J., C. Medcof and A.D. Tenant. 1971. Paralytic shellfish poisoning in eastern Canada. Bull. Fish. Res. Board Can. No. 177. pp. 1-86. (Cited in Carmichael *et al*. 1985.)

Prescott, G.W. 1948. Objectionable algae with reference to the killing of fish and other animals. Hydrobiologia 1: 1-13.

Ransom, R.E., T.A. Nerad and P.G. Meier. 1978. Acute toxicity of some blue-green algae to the protozoan *Paramecium caudatum*. J. Phycol. 14: 114-116. (Cited in Carmichael 1981.)

Reynolds, C.S. and A.E. Walsby. 1975. Water-blooms. Biol. Rev. 50: 437-481.

Rose, E.T. 1953. Toxic algae in Iowa lakes. Proc. Iowa Acad. Sci. 60: 738-745. (Cited in Moore 1977.)

Schantz, E.J. 1981. Poisons produced by dinoflagellates – a review. *In* The Water Environment: Algal Toxins and Health. W.W. Carmichael (ed.). Plenum Press, New York. pp. 25-36.

Schantz, E.J., J.M. Lynch, G. Vayvada, K. Matsumoto and H. Rapoport. 1966. The purification and characterization of the poison produced by *Gonyaulax catenella* in axenic culture. Biochemistry 5: 1191-1195. (Cited in Carmichael *et al*. 1985.)

Schantz, E.J., V.E. Ghazarossian, H.K. Schnoes, F.M. Strong, J.P. Springer, J.O. Pezzanite and J. Clardy. 1975. The structure of saxitoxin. J. Am. Chem. Soc. 97: 1238-1239. (Cited in Moore 1977.)

Schimizu, Y. 1977. Dinoflagellate toxins. *In* Marine Natural Products: New Perspectives. Vol. 1. P.J. Scheuer (ed.). Academic Press, New York. (Cited in Moore 1977.)

Schuett, W. and H. Rapoport. 1962. Saxitoxin, in the paralytic shellfish poison. Degradation to a pyrrolopyrimidine. J. Am. Chem. Soc. 84: 2266-2267. (Cited in Moore 1977.)

Senior, V.E. 1960. Algal poisoning in Saskatchewan. Can. J. Comp. Med. 24: 26-31.

Shilo, M. 1971. Toxins of Chrysophyceae. *In* Microbiological Toxins. S. Kadis, A. Ciegler and S. Ajl (eds.). Academic Press, London. pp. 67-103.

Snell, T.W. 1980. Blue-green algae and selection in Rotifer populations. Oecologia (Berlin) 46: 343-346. (Cited in Carmichael 1981.)

Sykora, J.L. and G. Keleti. 1981. Cyanobacteria and endotoxins in drinking water supplies. *In* The Water Environment: Algal Toxins and Health. W.W. Carmichael (ed.). Plenum Press, New York. (Cited in Carmichael *et al*. 1985.)

Tangen, K. 1977. Blooms of *Gyrodinium aureolum* (Dynophyceae) in north European waters, accompanied by mortality in marine organisms. Sarsia 63: 123-133.

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sulphate See Section 6.2.38.3 (see also sulphur)

sulphide See Section 6.2.38.4 (see also sulphur)
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surface active agents See surfactants
surfactants See Section 6.3.16
suspended solids See Section 6.4.8
2,4-D (2,4-dichlorophenoxyacetic acid) See Section 6.3.12.3.1
2,4,5-T See Section 6.3.12.3.2
2,4,5-TP See Section 6.3.12.3.3
2-propenal See acrolein
tannin See organic carbon
taste See Section 6.4.5
TCDD See polychlorinated dibenzo-*p*-dioxins
TDE See DDD
TDS See total dissolved solids
Temik See carbamate pesticides (aldicarb)
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tetrachlorobenzene See chlorinated benzenes
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Thiodan See endosulfan
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TIC See inorganic carbon (total inorganic carbon)
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total inorganic carbon See inorganic carbon
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toxaphene See Section 6.3.12.4.13
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TRC (total residual chlorine) See chlorine
tribromomethane See trihalomethanes
tributyltins See organotin compounds
trichlorobenzene See chlorinated benzenes
trichloroethane See chlorinated ethanes
trichloroethylene See chlorinated ethylenes
trichloromethane See trihalomethanes
trichlorophenol See chlorinated phenols
trihalomethanes See Section 6.3.4.7
trinitrobenzenes See nitrobenzenes
triophanate-methyl See carbamate pesticides
trinitrophenol See nitrophenols
tritium See radiological parameters
tungsten See Section 6.2.42
turbidity See Section 6.4.8
uranium See Section 6.2.43
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xylenol See monohydric and dihydric phenols
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Ziram See carbamate pesticides

APPENDIX I
GLOSSARY, SYMBOLS AND ABBREVIATIONS

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I.1 GLOSSARY

Abiotic: The nonliving components of a system (see biota).

Absorption: Chemical definition: penetration of one substance into the body of another.
Biological definition: the act of absorbing, i.e. to take in as fluids or gases through a cell membrane. To take a substance, e.g. water, nutrients, into the body through the skin or mucous membranes, or in plants, through root hairs.

Acclimation: (1) Steady-state compensatory adjustments by an organism to the alteration of environmental conditions. Adjustments can be behavioural or physiological/biochemical. (2) An adaptation of aquatic organisms to some selected experimental conditions, including adverse stimuli. (3) Acclimation also refers to the time period prior to the initiation of a toxicity test in which aquatic organisms are maintained in untreated, toxicant-free dilution water with physical and chemical characteristics (e.g. temperature, pH, hardness) similar to those to be used during the toxicity test.

Acid-soluble metal: The concentration of the metal that passes through a 0.45-µm membrane filter after the sample is acidified to pH 1.5-2.0 with nitric acid.

Acute: Having a sudden onset, lasting a short time. Of a stimulus, severe enough to induce a response rapidly. Can be used to define either the exposure or the response to an exposure (effect).

Acute:chronic ratio: The species mean acute value divided by the chronic value for the same species. The final acute:chronic ratio is the geometric mean of all acute:chronic ratios for species of aquatic animals in at least three different families provided that at least one is a fish, at least one is an invertebrate and at least one is an acutely sensitive freshwater species.

Acute value (final): An estimate of the concentration of the material corresponding to a cumulative probability of 0.05 in the acute toxicity values for the genera with which acceptable acute tests have been conducted.

Acute value (mean): The species mean acute value is the geometric mean of all appropriate (flow-through tests in which the concentrations have been measured, if available) 96-h (48-h for daphnids) LC_{50} or EC_{50} values for that species. The genus mean acute value is the geometric mean of the species mean acute values available for that genus.

Additive toxicity: The toxicity of a mixture of chemicals which is approximately equivalent to that expected from a simple summation of the known toxicities of the individual chemicals present in the mixture (i.e. algebraic summation of effects).

Adjuvant: An ingredient which, when added to a formulation, aids the action of the toxicant. The term includes such materials as wetting agents, spreaders, emulsifiers, dispersing agents, foaming agents, foam suppressants, penetrants and correctives.

Adsorption: The taking up of one substance at the surface of another.

Aeration: Any process where a substance becomes permeated with air or another gas. The term is usually applied to aqueous liquids being brought into intimate contact with air by spraying, bubbling or agitating the liquid.

Aerobe (aerobic): Organisms that can prosper only when oxygen is present more or less abundantly.

Aesthetic: Dealing with those aspects of water that are perceivable by the senses.

Agglomeration: See Suspension.

Air stripping: A technique for removal of volatile substances from a solution, normally by the use of large volumes of air.

Algae: Comparatively simple chlorophyll-bearing plants, most of which are aquatic and microscopic in size.

Alkalinity: The quantitative capacity of aqueous media to react with hydroxyl ions. The equivalent sum of the bases that are titratable with strong acid. Alkalinity is a capacity factor that represents the acid-neutralizing capacity of an aqueous system.

Amperometric method: A special adaptation of the polarographic principle involving a titration at pH range of 6.5-7.5 and a second titration in the presence of potassium iodide at a pH range of 3.5-4.5.

Amphipod: Invertebrates belonging to the order of Crustacea including the freshwater shrimps.

Anaerobe (anaerobic): Organisms which either by obligation or facultatively thrive in the absence of oxygen.

Antagonism: A phenomenon in which the toxicity of a mixture of chemicals is less than that which would be expected from a simple summation of the toxicities of the individual chemicals present in the mixture (i.e. algebraic subtraction of effects).

Application factor (AF): A numerical, unitless value, calculated as the threshold chronically toxic concentration of a chemical divided by its acutely toxic concentration. An AF is generally calculated by dividing the limits [no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC)] on the maximum acceptable toxicant concentration (MATC) by the time-independent LC_{50}, if available, or the 96-h LC_{50} (or 48-h EC_{50} or 48-h LC_{50} for daphnids) from a flow-through acute toxicity test. The AF is usually reported as a range and is multiplied by the median lethal concentration of a chemical as determined in a short-term (acute) toxicity test to estimate an expected no-effect concentration under chronic exposure.

Assimilation: The incorporation of absorbed substances into cellular material.

Avoidance threshold: The lowest concentration of a substance that causes a fish to actively move away from the source.

Benthic: Referring to organisms living in or on the sediments of aquatic habitats (lakes, rivers, ponds, etc.).

Benthos: The sum total of organisms living in, or on, the sediments of aquatic habitats.

Bioaccumulation: General term describing a process by which chemical substances are accumulated by aquatic organisms from water directly or through consumption of food containing the chemicals.

Bioassay: Test used to evaluate the relative potency of a chemical by comparing its effect on a living organism with the effect of a control, without the test chemical, which is run under identical conditions.

Bioavailable: The fraction of the total chemical in the surrounding environment which can be taken up by organisms. The environment may include water, sediment, suspended particles, and food items.

Biochemical oxygen demand (BOD): The decrease in oxygen content in milligrams per litre of a sample of water in the dark at a certain temperature over a certain period of time, which is brought about by the bacterial breakdown of organic matter. Usually the decomposition has proceeded so far after 20 d that no further change occurs. The oxygen demand is measured after 5 d (BOD_5), at which time 70% of the final value has usually been reached.

Bioconcentration: A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g. by gill or epithelial tissue) and elimination.

Bioconcentration factor (BCF): A unitless value describing the degree to which a chemical can be concentrated in the tissues of an organism in the aquatic environment. At apparent equilibrium during the uptake phase of a bioconcentration test, the BCF is the concentration of a chemical in one or more tissues of the aquatic organisms divided by the average exposure concentration in the test.

Biological monitoring: The direct measurement of changes in the biological status of a habitat based on evaluations of the number and distribution of individuals or species before and after a change.

Biomagnification: Result of the processes of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels. The term implies an efficient transfer of chemicals from food to consumer, so that residue concentrations increase systematically from one trophic level to the next.

Biomass: The living weight of a plant or animal population, usually expressed on a unit area basis.

Biota: The sum total of the living organisms of any designated area.

Bioturbation: The physical disturbance of sediments by burrowing and other activities of organisms.

Bloom: An unusually large number of organisms per unit of water, usually algae, made up of one or a few species.

Buffer: A solution containing a weak acid and its conjugate weak base whose pH changes only slightly on the addition of acid or alkali.

Calcium sulphate product: A scaling index used to estimate the upper limit of calcium and sulphate concentrations in circulating water of a cooling system and expressed as $[Ca^{2+}] \times [SO_4^{2-}] = 500\,000$.

Carcinogen: A substance which induces cancer in a living organism.

Cation-exchange capacity: The total quantity of cations which a soil can adsorb by cation exchange, usually expressed as milliequivalents per 100 grams. Measured values of cation-exchange capacity depend somewhat on the method used for the determination.

Chelate: The type of coordination compound in which a central metal ion is attached by coordinate links to two or more nonmetal atoms in the same molecule, called ligands.

Chemosynthesis: The synthesis of organic matter from inorganic compounds, using simple inorganic reactions as a source of energy.

Chlorination: (1) The process of introducing one or more chlorine atoms into a compound. (2) The application of chlorine to water, sewage or industrial wastes for disinfection or other biological or chemical results.

Chlorophyll: The green pigments of plants.

Chronic: Involving a stimulus that is lingering or continues for a long time; often signifies periods from several weeks to years, depending on the reproductive life cycle of the aquatic species. Can be used to define either the exposure or the response to an exposure (effect). Chronic exposure typically induces a biological response of relatively slow progress and long continuance.

Chronic test: See Life cycle study.

Chronic value: The geometric mean of the lower and upper limits from an acceptable chronic test or by analyzing chronic data using a regression analysis. A lower chronic limit is the highest tested concentration which did not cause an unacceptable amount of adverse effect on any of the specified biological measurements, and below which no tested concentration caused unacceptable effect. An upper chronic limit is the lowest tested concentration which did cause an unacceptable amount of adverse effect on one or more biological measurements and above which all tested concentrations also caused such an effect.

Cladoceran: Water flea. Zooplankton belonging to the fourth order of the Branchiopoda, the Cladocera.

Coagulation: The process of converting a finely divided or colloidally dispersed suspension of a solid into particles of such size that settling takes place.

Colloid: A state of matter intermediate between a true solution and a suspension where the material is typically 0.1 μm to 1 nm in diameter. Colloids (colloidal particles) cannot settle out of a circulating medium through the force of gravity. Colloidal particles cannot diffuse through membranes which do allow ordinary molecules and ions to pass freely.

Community: An assemblage of organisms characterized by a distinctive combination of species occupying a common environment and interacting with one another.

Compensation point: The depth at which assimilation and dissimilation are equal (see assimilation).

Concentration: The quantifiable amount of chemical in the surrounding water, food or sediment.

Condensation: (1) A chemical change in which two or more molecules react with the elimination of water or some other simple substance. (2) The change of a vapour into a liquid, which occurs when the pressure of the vapour becomes equal to the maximum vapour pressure of the liquid at that temperature.

Congenital: Dating from birth or from before birth.

Control: A treatment in a toxicity test that duplicates all the conditions of the exposure treatments but contains no test material. The control is used to determine the absence of toxicity in the basic test conditions (e.g. health of test organisms, quality of dilution water).

Corrosion: The electrochemical degradation of metals or alloys due to reaction with their environment; it is accelerated by the presence of acids or bases.

Criteria (water quality): Scientific data evaluated to derive the recommended limits for water uses.

Cumulative: Brought about, or increased in strength, by successive additions at different times or in different ways.

Cyanide, weak acid dissociable: The concentration of HCN following distillation of the sample in the presence of acetate buffer at pH 4.5. This method measures free, simple and weak-acid-dissociable metal cyanides.

Delayed effects: Effects or responses that occur some time after exposure.

Demersal: Living in the lowest layer of a sea or lake. Sometimes used as a synonym for "benthic".

Depuration: A process that results in elimination of a material from an aquatic organism.

Detection limit: The smallest concentration or amount of a substance which can be reported as present with a specified degree of certainty by a definite, complete analytical procedure.

Detritus: Unconsolidated sediments composed of both inorganic and dead and decaying organic material.

Dilution water (diluent): Water used to dilute the test material in an aquatic toxicity test in order to prepare either different concentrations of a test chemical or different percentages of an effluent for the various test treatments.

Dimictic lake: Lake that circulates freely twice a year in the spring and fall and is directly stratified in summer, inversely stratified in winter. Dimictic lakes represent the most common type of thermal stratification observed in most lakes of the cool temperate regions of the world.

Dissociation: The splitting of a molecule of a substance (a salt, acid or base) existing in solution into electrically charged particles (ions). The positively charged hydrogen ion and metallic ions are called cations; the negatively charged hydroxyl ion and acid ions are called anions.

Dissolved constituent: The constituents in a water sample that will pass through a 0.45-μm membrane filter.

Diurnal: Daily.

Diurnal cycling: Having a period of variation of one day.

Dose: The quantifiable amount of a material introduced into an animal.

Dynamic equilibrium: See Steady state.

EC_{50}: See Median effective concentration.

Early life-stage test: 28- to 32-d (60 d posthatch for salmonids) exposures of the early life stages of a species of fish from shortly after fertilization through embryonic, larval and early juvenile development. Data are obtained on survival and growth.

Effluent: A complex waste material (e.g. liquid industrial discharge or sewage) which may be discharged into the environment.

Epilimnion: The uppermost layer of water in a lake, characterized by an essentially uniform temperature, that is generally warmer than elsewhere in the lake, and by relatively uniform mixing by wind and wave action.

Epiphyte: A plant which grows on the outside of another plant, using it for support only and not obtaining food from it.

Eutrophic: Abundant in nutrients and having high rates of productivity frequently resulting in oxygen depletion below the surface layer of a water body.

Evapotranspiration: The combined loss of material from a given area during a specified period of time by evaporation from the soil or water surface and by transpiration from plants.

Exposure: The amount of a physical or chemical agent that reaches a target or receptor.

Fate: Disposition of a material in various environmental compartments (e.g. soil or sediment, water, air, biota) as a result of transport, transformation and degradation.

Field capacity: The greatest amount of water that is possible for a soil to hold in its pore spaces after excess water has drained away.

Flocculation: (1) The process by which suspended colloidal or very fine particles coalesce and agglomerate into well-defined hydrated floccules of sufficient size to settle rapidly. (2) The stirring of water after coagulant chemicals have been added to promote the formation of particles that will settle.

Flow-through system: An exposure system for aquatic toxicity tests in which the test material solutions and control water flow into and out of test chambers on a once-through basis either intermittently or continuously.

Guideline (water quality): Numerical concentration limit or narrative statement recommended to support and maintain a designated water use.

Half-life: Time required to reduce by one-half the concentration of a material in a medium (e.g. soil or water) or organism (e.g. fish tissue) by transport, degradation, transformation or depuration.

Halogenation: The incorporation of a halogen (usually chlorine or bromine) into a chemical compound.

Hardness: The concentration of all metallic cations, except those of the alkali metals, present in water. In general, hardness is a measure of the concentration of calcium and magnesium ions in water and is frequently expressed as milligrams per litre calcium carbonate equivalent.

Hazard evaluation: Identification and assessment of the potential adverse effects that could result from manufacture, use and disposal of a material in a specified quantity and manner.

Hectare: Metric unit of area; 100 hectares = 1 km^2; 1 hectare = 2.47 acres.

Henry's constant: The mass of a gas dissolved in a solvent is proportional to the pressure of the gas with which it is in equilibrium.

Heterotrophy: The nutrition of plants and animals that are dependent on organic matter for food.

Holomictic lake: Lake in which circulation occurs throughout the entire water column.

Humic acid: See Humic substances.

Humic substances: Organic substances only partially broken down, which occur in water mainly in a colloidal state. Humic acids are large-molecule organic acids that dissolve in water.

Hydrogenation: Any reaction of hydrogen with an organic compound. For example, the hydrogenation of unsaturated vegetable oils to solid fats by addition of hydrogen to their double bonds.

Hydrolysis: (1) The formation of an acid and a base from a salt by the ionic dissociation of water. (2) The decomposition of organic compounds by interaction with water.

Hypolimnion: The region of a body of water that extends from below the thermocline to the bottom of the lake; it is, thus, removed from much of the surface influence.

Hypoxia: Deficiency of oxygen in tissues or in blood. Anoxia.

In vitro: Outside the intact organism; generally applied to experiments involving biochemical events occurring in tissue fragments or fractions.

In vivo: Within an intact animal or organism.

Incipient LC$_{50}$: The concentration of a chemical which is lethal to 50% of the test organisms as a result of exposure for periods sufficiently long that acute lethal action has essentially ceased. The asymptote (part of the toxicity curve parallel to the time axis) of the toxicity curve indicates the value of the incipient LC$_{50}$, approximately.

Ingestion: The swallowing or taking in of food material.

Interstitial: Occurring in interstices or spaces, applied to water found between, and to flora and fauna living between sand grains and soil particles.

Invertebrates: Animals lacking a dorsal column of vertebrae or a notochord.

Ion: See Dissociation.

Ionization: The process whereby atoms acquire an electrical charge through the gain or loss of electrons.

Joint action: Two or more chemicals exerting their effects simultaneously.

LC$_{50}$: See Median lethal concentration.

Langelier Saturation Index (SI): Index relating the actual pH of water (pH) to the pH at which water is just saturated with calcium carbonate (pH$_s$). SI = pH – pH$_s$.

Leaching: The downward movement of a material in solution through soil.

Lethal: Causing death by direct action. Death of aquatic organisms is the cessation of all visible signs of biological activity.

Lethal time: See Survival time.

Life cycle study: A chronic (or full chronic) study in which all the significant life stages of an organism are exposed to a test material. Generally, a life cycle test involves an entire reproductive cycle of the organism. A partial life cycle toxicity test includes the part of the life cycle observed to be especially sensitive to chemical exposure.

Ligand: A molecule, ion or atom that is attached to the control atom of a coordination compound, a chelate or other complex. May also be called complexing agent.

Limnology: The study of fresh water, including biological, geological, physical and chemical aspects.

Lipophilic: Having an affinity for fats or other lipids.

Littoral zone: The interface region between the land of the draining basin and the open water of lakes.

Loading: (1) Ratio of the animal biomass to the volume of test solution in an exposure chamber. (2) In limnology, the amount of a substance added per unit of lake area per unit time.

Lordosis: An anteroposterior curvature of the spine, generally in the lumbar region.

Lowest observed effect concentration (LOEC): The lowest concentration of a material used in a toxicity test that has a statistically significant adverse effect on the exposed population of test organisms as compared with the controls. When derived from a life cycle or partial life cycle test, it is numerically the same as the upper limit of the MATC.

Macrophyte: A member of the macroscopic plant life especially of a body of water.

Macroscopic: Large enough to be observed by the naked eye.

Marl: An earthy, unconsolidated deposit formed in freshwater lakes, consisting chiefly of calcium carbonate mixed with clay or other impurities in varying proportions.

Maximum acceptable toxicant concentration (MATC): The concentration of a toxic substance that may be present in a receiving water without causing significant harm to its productivity or uses as determined by chronic toxicity tests.

Measured flow-through test: A toxicity test with constant flow or continuous flow of water where the concentration of the substance in the water is measured.

Median effective concentration (EC$_{50}$): The concentration of material in water to which test organisms are exposed that is estimated to be effective in producing some sublethal response in 50% of the test organisms. The EC$_{50}$ is usually expressed as a time-dependent value (e.g. 24-h or 96-h EC$_{50}$).

Median effective dose (ED$_{50}$): The dose of material estimated to be effective in producing some sublethal response in 50% of the test organisms. It is appropriately used with test animals such as rats, mice and dogs, but it is rarely applicable to aquatic organisms because it indicates the quantity of a material introduced directly into the body by injection or ingestion rather than the concentration of the material in water in which aquatic organisms are exposed during toxicity tests.

Median lethal concentration (LC_{50}): The concentration of material in water to which test organisms are exposed that is estimated to be lethal to 50% of the test organisms. The LC_{50} is usually expressed as a time-dependent value (e.g. 24-h or 96-h LC_{50}; the concentration estimated to be lethal to 50% of the test organisms after 24 or 96 h of exposure).

Median lethal dose (LD_{50}): The dose of material that is estimated to be lethal to 50% of the test organisms. It is appropriately used with test animals such as rats, mice and dogs, but it is rarely applicable to aquatic organisms because it indicates the quantity of a material introduced directly into the body by injection or ingestion rather than the concentration of the material in water in which aquatic organisms are exposed during toxicity tests.

Median tolerance limit (TL_m or TL_{50}): The concentration of material in water at which 50% of the test organisms survive after a specified time of exposure. The TL_{50} (equivalent to the TL_m) is usually expressed as a time-dependent value (e.g. 24-h or 96-h TL_{50}; the estimated concentration at which 50% of the test organisms survive after 24 or 96 h of exposure). Unlike lethal concentration and lethal dose, the term tolerance limit is applicable in designating a level of any measurable lethal condition (e.g. extremes in pH, temperature, dissolved oxygen). TL_m and TL_{50} have been replaced by median lethal concentration (LC_{50}) and median effective concentration (EC_{50}).

Meromictic lake: Lake that at the time of winter cooling undergoes only a partial circulation down to a depth determined by a density stratification.

Metabolism: The sum of all chemical processes occurring in an organism or living cell.

Metabolite: Any product of metabolism.

Metalimnion: The layer of water in a lake between the epilimnion and hypolimnion in which the temperature exhibits the greatest difference in a vertical direction.

Methylation: The introduction of methyl (CH_3) groups into organic and inorganic compounds.

Mineralize: To convert to a mineral substance; to impregnate with mineral material.

Mutagenesis: The alteration of the genetic material of a cell in such a manner that the alteration is transmitted to subsequent generations of cells.

Nannoplankton: Those organisms suspended in open water which because of their small size cannot be collected by nets. They can be recovered by sedimentation or centrifugation.

Nekton: The powerful swimmers among the freshwater animals that to a large degree are capable of moving about voluntarily from place to place.

Neuston: The collective term for microscopic components of the pleuston that are adapted to the interface habitat between air and water. The neuston are classified as those organisms adapted to living on the upper surface of the interface film (the epineuston) and those living on the underside of the surface film (the hyponeuston).

Not detectable: Below the limit of detection of a specified method of analysis.

Objective (water quality): A numerical concentration limit or narrative statement which has been established to support and protect the designated uses of water at a specified site.

Octanol-water partition coefficient (P_{ow}): The ratio of a chemical's solubility in *n*-octanol and water at equilibrium. The logarithm of P_{ow} is used as an indication of a chemical's propensity for bioconcentration by aquatic organisms.

Oligotrophic: Waters with a small supply of nutrients.

Organism: Any living animal or plant; anything capable of carrying on life processes.

Organoleptic: Pertaining to or perceived by a sensory organ.

Osmosis: Diffusion of a solvent through a semipermeable membrane into a more concentrated solution, tending to equalize the concentrations on both sides of the membrane.

Oxidation: The combination of oxygen with a substance, or the removal of hydrogen from it or, more generally, any reaction in which an atom loses electrons.

Oxygenation: The process of adding dissolved oxygen to a solution.

Parameter: A measurable or quantifiable characteristic or feature.

Partition coefficient: A ratio of the equilibrium concentration of the chemical between a nonpolar and polar solvent.

Pathogen: An organism capable of eliciting disease symptoms in another organism.

Pelagic: Term applied to organisms of the plankton and nekton which inhabit the open water of a sea or lake.

Periphyton: The organisms attached to submerged plants.

Pesticide: A substance or mixture of substances used to kill unwanted species of plants or animals.

pH: Value taken to represent the acidity or alkalinity of an aqueous solution. It is defined as the negative logarithm of the hydrogen ion acidity of the solution.

Photolysis: The decomposition of a compound into simpler units as a result of absorbing one or more quanta of radiation.

Photooxidation: Oxidation induced by radiant energy.

Photosynthesis: The conversion of carbon dioxide to carbohydrates in the presence of chlorophyll using light energy.

Physiology: The study of the functioning of organisms and their parts.

Pinocytosis: The ingestion of drops of liquid by cells.

Plankton: Plants (phytoplankton) and animals (zooplankton), usually microscopic, floating in aquatic systems.

Pleuston: Specialized organisms that are adapted to the interface habitat between air and water.

Poikilothermy: The possession of a body temperature which varies, approximating to that of the surroundings. Cold-bloodedness.

Polymerization: A chemical reaction, usually carried out with a catalyst, heat or light, and often under high pressure, in which a large number of relatively simple molecules combine to form a chain-like macromolecule.

Potable water: Water suitable, on the basis of both health and aesthetic considerations, for drinking or culinary purposes.

Precipitation: (1) The formation of solid particles in a solution. Generally, the settling out of small particles. (2) The settling out of water from cloud, in the form of rain, hail, snow, etc.

Primary production: The production of organic matter from inorganic materials.

Producers: Organisms that are able to build up their body substance from inorganic materials.

Purge: The removal of volatile or dissolved substances through intense agitation or aeration.

Range: The difference between the lowest and highest values in a set of data.

Raw water: Surface or groundwater that is available as a source of drinking water but has not received any treatment.

Reduction: The removal of oxygen from a substance or the addition of hydrogen to it. Generally, any reaction in which an atom gains electrons.

Resistance time: The period of time for which an aquatic organism can live beyond the incipient lethal level.

Risk: A statistical concept defined as the expected frequency or probability of undesirable effects resulting from a specified exposure to known or potential environmental concentrations of a material. A material is considered safe if the risks associated with its exposure are judged to be acceptable. Estimates of risk may be expressed in absolute or relative terms. Absolute risk is the excess risk due to exposure. Relative risk is the ratio of the risk in the exposed population to the risk in the unexposed population.

Ryzner Stability Index (RSI): Index relating the pH of water (pH) to the pH of water just saturated with calcium carbonate (pH_s). $RSI = 2pH_s - pH$.

Safety factor: A number used to provide an extra margin of safety beyond the known or estimated sensitivities of aquatic organisms. Often applied when sufficient information about the toxicity, particularly the chronic toxicity, of a particular substance is not well known.

Scale: A calcareous deposit in water tubes or steam boilers resulting from deposition of mineral compounds present in the water.

Scoliosis: Lateral curvature of the spine.

Seston: All the particulate matter suspended in water.

Sizing compound: A material such as starch, gelatin, casein, gums, oils, waxes, asphalt emulsions, silicones, rosin and water-soluble polymers applied to yarns, fabrics, paper, leather and other products to improve or increase their stiffness, strength, smoothness or weight.

Solvent: An agent (other than water) in which the test chemical is mixed to make it miscible with dilution water before distribution to test chambers.

Sorption: A surface phenomenon which may be either absorption or adsorption, or a combination of the two. The term is often used when the specific mechanism is not known.

Species: Generally regarded as a group of organisms which resemble each other to a greater degree than members of other groups and which form a reproductively isolated group that will not normally breed with members of another group.

Spray drift: The movement of airborne spray particles from the intended area of application.

Standard (water quality): An objective that is recognized in enforceable environmental control laws of a level of government.

Standing crop: The weight of organic material that can be sampled or harvested by normal methods at any one time from a given area.

Static system: An exposure system of aquatic toxicity tests in which the test chambers contain solutions of the test material or control water which are not usually changed during the test. Depending upon conditions, a static system may or may not be in equilibrium.

Steady state or dynamic equilibrium: The state at which the competing rates of uptake and elimination of a chemical within an organism or tissue are equal. An apparent steady state is reached when the concentration of a chemical in tissue remains essentially constant during a continuous exposure.

Stoichiometric weight: The relative quantities of elements in a chemical compound according to their combining weights.

Sublethal: Involving a stimulus below the level that causes death.

Sublittoral: The shore zone from the lowest water level to the lower boundary of plant growth.

Survival time: The time interval between initial exposure of an aquatic organism to a harmful parameter and death.

Suspended constituent: The constituents in a water sample (the residue) that are retained on a filter medium. The type of filter must be specified.

Suspension: A system in which very small particles (solid, semisolid, or liquid) are more or less uniformly dispersed in a liquid or gaseous medium. If the particles are small enough to pass through filter membranes, the system is termed a colloidal suspension. If the particles are larger than colloidal dimensions they will tend to precipitate, if heavier than the suspending medium, or to agglomerate and rise to the surface, if lighter.

Synergism: A phenomenon in which the toxicity of a mixture of chemicals is greater than that which would be expected from a simple summation of the toxicities of the individual chemicals present in the mixture.

TL_{50} (TL_m): See Median tolerance limit.

Tegument (Integument): An enveloping layer (as a skin, membrane or husk) of an organism or one of its parts.

Teratogen: An agent that increases the incidence of congenital malformations.

Thermocline: See Metalimnion.

Threshold concentration: A concentration above which some effect (or response) will be produced and below which it will not.

Tolerance: The ability of an organism to withstand adverse or other environmental conditions for an indefinitely long exposure without dying.

Tortuosity: The ratio of the length of the sinuous diffusion path (of solute) to the straight-line distance between its ends. Applies to a porous medium, such as sediment.

Total metal: The concentration of a metal in an unfiltered sample that is digested in strong nitric acid.

Total recoverable metal: The concentration of a metal in an unfiltered sample following treatment with hot dilute mineral acid.

Total recoverable method: An analytical method in which an unfiltered sample is treated with hot dilute mineral acid.

Toxicant: An agent or material capable of producing an adverse response (effect) in a biological system, seriously injuring structure or function or producing death.

Toxicity: The inherent potential or capacity of a material to cause adverse effects in a living organism.

Toxicity test: The means by which the toxicity of a chemical or other test material is determined. A toxicity test is used to measure the degree of response produced by exposure to a specific level of stimulus (or concentration of chemical).

Toxic unit: The strength of a chemical (measured in some unit) expressed as a fraction or proportion of its lethal threshold concentration (measured in the same unit). The strength may be calculated as follows:

$$\text{toxic unit} = \frac{\text{actual concentration of chemical in solution}}{\text{lethal threshold concentration}}$$

If this number is greater than 1.0, more than half of a group of aquatic organisms will be killed by the chemical. If it is less than 1.0, half the organisms will not be killed. 1.0 toxic unit = the incipient LC_{50}.

True colour: The colour of water resulting from substances which are totally in solution; not to be mistaken for apparent colour resulting from colloidal or suspended matter.

Turbulence: Unorganized movement in liquids and gases resulting from eddy formation.

Uptake: A process by which materials are absorbed and incorporated into a living organism.

U.S. FDA action level: The concentration of a toxic substance in an organism (often the edible portions of fish) that the U.S. Food and Drug Administration deems unacceptable for human consumption.

Van't Hoff's Law: A chemical reaction proceeds approximately twice as fast at a temperature increase of 10 C°.

Viscosity: The internal resistance to flow exhibited by a fluid.

Volatile: Having a low boiling or subliming pressure (a high vapour pressure).

Xenobiotic: A foreign chemical or material not produced in nature and not normally considered a constitutive component of a specified biological system. This term is usually applied to manufactured chemicals.

Zeolite: A natural hydrated silicate of aluminum and either sodium or calcium or both; or of an artificial ion-exchange resin. Both natural and artificial zeolites are used extensively for water softening and as detergent builders.

Zooplankton: The animal portion of the plankton.

I.2 SYMBOLS AND ABBREVIATIONS

Throughout the text the International System (SI) notation for units has been used.

SI PREFIXES

Prefix	Multiplying Factor	Symbol
mega	1 000 000 = 10^6	M
kilo	1 000 = 10^3	k
hecto	100 = 10^2	h
deca	10 = 10^1	da
	1 = 10^0	
deci	0.1 = 10^{-1}	d
centi	0.01 = 10^{-2}	c
milli	0.001 = 10^{-3}	m
micro	0.000 001 = 10^{-6}	μ
nano	0.000 000 001 = 10^{-9}	n
pico	0.000 000 000 001 = 10^{-12}	p

Time		Mass	
a	annum	g	gram
d	day	kg	kilogram
h	hour	mg	milligram
s	second	μg	microgram
min	minute	ng	nanogram
		wt	weight
		t	tonne

Volume		Area	
L	litre	ha	hectare
mL	millilitre		

Length		Power	
m	metre	W	Watt
km	kilometre	kW	kilowatt

Temperature		Pressure	
°C	degree Celsius	Pa	pascal
		kPa	kilopascal

Other Abbreviations

$mol \cdot L^{-1}$	moles per litre
μmol	micromoles
pK_a	logarithm of the acid dissociation constant
P_{ow}	octanol/water partition coefficient
K_d	soil sorption coefficient
K_{oc}	organic carbon sorption coefficient
$\mu S \cdot cm^{-1}$	microsiemens per centimetre
a.i.	active ingredient

I.3 BIBLIOGRAPHY

Allaby, M. 1983. A Dictionary of the Environment. 2nd edition. New York University Press, New York. 529 pp.

Drever, J.I. 1982. The Geochemistry of Natural Waters. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 388 pp.

Environment Canada. 1979. Analytical Methods Manual. Water Quality Branch, Inland Waters Directorate, Ottawa.

Hawley, G.G. 1981. The Condensed Chemical Dictionary. 10th edition. Van Nostrand Reinhold Co., New York. 1135 pp.

Lewis, W.H. 1977. Ecology Field Glossary. A Naturalist's Vocabulary. Greenwood Press, Westport, Connecticut. 152 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa. 88 pp.

Neely, W.B. 1980. Chemicals in the Environment. Distribution. Transport. Fate. Analysis. Marcel Dekker, Inc., New York. 245 pp.

Rand, G.M. and S.R. Petrocelli (eds.). 1985. Fundamentals of Aquatic Toxicology. Methods and Applications. McGraw-Hill International Book Co., New York. 666 pp.

Rogers, B.G., W.T. Ingram, E.H. Pearl and L.W. Welter. 1981. Glossary. Water and Wastewater Control Engineering. 3rd edition. American Public Health Association, American Society of Civil Engineers, American Water Works Association, Water Pollution Control Federation. Washington, D.C. 441 pp.

Ruttner, F. 1963. Fundamentals of Limnology. University of Toronto Press. Toronto, Ontario. 295 pp.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2nd edition. John Wiley & Sons, New York. 780 pp.

Trudinger, P.A. and D.J. Swaine. 1979. Biogeochemical Cycling of Mineral-forming Elements. Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. 612 pp.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033. 594 pp.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. 2nd edition. Van Nostrand Reinhold Co., New York. 1310 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

APPENDIX II

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APPENDIX II

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APPENDIX IV

FACTORS TO CONSIDER WHEN USING THE CANADIAN GUIDELINES TO DEVELOP SITE-SPECIFIC WATER QUALITY OBJECTIVES

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APPENDIX IV

FACTORS TO CONSIDER WHEN USING THE CANADIAN GUIDELINES TO DEVELOP SITE-SPECIFIC WATER QUALITY OBJECTIVES

IV.1 INTRODUCTION

The Canadian Water Quality Guidelines provide basic scientific information on the effects of water quality parameters on uses in order to assess present and potential water quality issues and concerns and to develop water quality objectives for specific sites.

Water quality is affected in different ways by local variations in physical, chemical and biological conditions. Environmental assessments involve the measurement of a parameter in one or more media (e.g. water, sediment, biota) or the measurement of the effect of a parameter for the purpose of assessing and providing recommendations for controlling exposure (UNEP 1985). They are used to compare and interpret long-term information on ambient water quality conditions and changes in these conditions. The information is also used, together with the recommendations and conditions described in the water quality guidelines for each use, in formulating site-specific water quality objectives. The objectives serve as a reference point to assess and interpret changes in water quality conditions and impacts on water uses. They are also used in designing environmental assessments to address special concerns.

Many of the guidelines recommended in the Canadian Water Quality Guidelines will be modified, when used to formulate water quality objectives, to account for site-specific variations in conditions. The guidelines should therefore not be regarded as blanket values for national water quality. Their use requires an understanding of the chemical, physical and biological characteristics of the water body and an understanding of the behaviour of a substance once it is introduced into the aquatic environment.

The following discussion highlights some of the factors that affect the application of the guidelines, that is, (1) the general characteristics of lakes, rivers and groundwater; (2) the effect of local environmental conditions on water quality; (3) processes affecting the concentration of parameters in water and (4) factors that modify toxicity to aquatic organisms.

It is beyond the scope of this document to present a detailed and complete review of all the information related to the application of the guidelines. Its purpose is to give the reader a greater appreciation of the complex chemical, physical and biological interactions which take place in lakes, rivers and groundwaters, and affect the use of the guidelines and the development of water quality objectives. Not all factors will apply to a given situation and users of this document are strongly encouraged to consider the rationale for each guideline and to consult with specialists in the field of water quality.

IV.2 CHARACTERISTICS OF AQUATIC SYSTEMS

IV.2.1 Lakes

Lakes with surface outlets can be regarded as holding and mixing basins for the streamflow that results. The holding time of water in a lake provides the opportunity for sedimentation and for slow reactions to progress further than they would in a flowing river system (Hem 1985).

Most temperate lakes are stratified on a seasonal basis. During the winter, the lakes are covered with ice. Winter stagnation can develop with water temperatures of 0°C directly below the ice and uniformly low temperatures at, or slightly above, 4°C in the deeper waters. After ice break-up, wind action on the surface water results in mixing of the entire water mass (spring overturn). The lake becomes isothermal and chemically homogeneous (Birge and Juday 1921).

In the spring, heat energy is absorbed by the upper layers of the lake. The main energy source that distributes heat in a lake is the wind. It generates currents which move surface waters; a countercurrent develops below the surface which leads to heat exchange. Density gradients are formed in sufficiently deep lakes by the accumulation of heat. A boundary layer (thermocline) develops between the mixed surface layer (epilimnion) and the cooler and less mixed water mass (hypolimnion) (Birge 1910).

In the fall, cooler temperatures result in changes in water density and the breakdown of thermal stratification. By late fall, isothermal conditions develop and the lake is mixed again (autumn overturn).

The thermocline is very important to the biology of a lake. It acts as a barrier to the movement of dissolved oxygen, solutes, toxicants and the distribution of heat between the epilimnion and the hypolimnion (Reid and Wood 1976). Photosynthesis occurs mainly but not exclusively in the upper layers of a lake (trophogenic layer). The process is governed by factors dependent on the species of phytoplankton present, light penetration, nutrient availability, temperature and the interrelationships among phytoplankton requirements. The organic matter that results settles out of the trophogenic zone and enters the deep tropholytic layer. The movement of organic matter and its subsequent biodegradation results in decreased dissolved oxygen levels in the hypolimnion. The chemical oxidation of the organic matter also affects concentrations of dissolved oxygen (Kwiatkowski 1984). The thermocline constitutes a barrier between the epilimnion and hypolimnion to the movement of dissolved gases. In the hypolimnion, if oxygen levels relative to organic input are large, it will remain oxygenated. Alternatively, if oxygen levels are low, the hypolimnion could become anaerobic. Under these conditions, the biological community (benthos, zooplankton, bacteria, fish) and water chemistry are affected (e.g. accumulation of inorganic matter, release of nutrients and sorbed metals) (Connell and Miller 1984).

The terms oligotrophic, mesotrophic and eutrophic describe the general productivity of a lake. Oligotrophic refers to waters with low nutrient content and low biological activity. Mesotrophic refers to waters with average productivity. Eutrophic refers to highly productive waters with high nutrient levels (Drever 1982; Waite 1984). Eutrophication results in changes in the species composition of some phytoplankton, increases in turbidity and colour, and decreases in concentrations of dissolved oxygen as a result of plant death and decomposition (Connell and Miller 1984).

The water regime of many lakes is controlled by their tributaries. They connect a lake both geochemically and biologically with its catchment area. The impact of tributaries on lake conditions will be a function of their inflow rate relative to the water budget of the lake and the degree of mixing of the incoming waters with the lake waters. The inflow water will tend to flow into the lake depth that most closely matches its density according to temperature and dissolved and suspended materials (Frevert 1985). These relationships will change seasonally because of stratification effects in the lake. In lakes with a low flushing rate, the chemical composition will also be affected by precipitation and by the rate of evapotranspiration.

IV.2.2 Rivers and Streams

The character of rivers and streams is determined by current velocity. The velocity depends on the width, depth and gradient of the stream or river, the roughness of the bed and seasonal variations in the flow rate. Velocity plays a major role in influencing the distribution of dissolved substances, the quantity of sediment (silt, sand, clay and organic matter) in suspension and in the process of settling, the bed composition and the development, distribution and stability of the biotic community (Reid and Wood 1976).

The transport of materials in water depends primarily on advection and dispersion. Advection refers to movement of dissolved or fine particulate matter at the velocity of the current in the longitudinal, lateral or vertical directions. Dispersion refers to the process by which these substances are mixed within the water column (Neely and Blau 1985b). Heavier substances will be subjected to the effects of current, but will undergo additional transport, such as sedimentation. The turbulence in flowing waters is not uniform and contributes greatly to the unstable nature of bottom sediments.

The chemical content of flowing waters varies greatly from one area to another, and is a reflection of local geography, seasonality, runoff and biological processes (Bowen 1979). The relative concentration, composition and longitudinal distribution of dissolved solids in rivers will differ from those in lakes because of differences in water volume, surface-to-volume ratio and mixing characteristics, which are subject to changes in flow rather than stratification (Horne 1978).

The temperature in streams is determined by factors such as current velocity, volume, depth, cover, water source and seasonal and diurnal variations. Vertical thermal stratification is not generally observed in rivers largely because turbulent streamflow assures good vertical mixing (Hynes 1970).

The oxygenation of flowing waters occurs primarily by physical aeration and photosynthesis. The contribution of each of these sources varies depending on the time of day, the season, current velocity, bed morphology, temperature and biological factors. The rate of physical aeration in rivers is largely determined by temperature, degree of turbulence, depth and oxygen demand. A discharge of organic matter, for example, will cause a decrease in dissolved oxygen concentrations brought on by increased microbial respiration. Replenishment occurs by adsorption of atmospheric oxygen at the air-water interface. Photosynthetic contributions to dissolved oxygen concentrations are more noticeable under less turbulent conditions, where algae and higher plants have had an opportunity to produce oxygen. Photosynthetic processes, however, are subject to diurnal and seasonal fluctuations (Reid and Wood 1976).

IV.2.3 Groundwater

Groundwater occurs below the water table in permeable geologic formations (aquifers). It is recharged by deep percolation from precipitation, irrigation and water spreading, by seepage from streams and lakes, and by recharge from recharge wells. It emerges naturally in the form of springs or as seepage to streams, ponds or lakes (U.S. Department of the Interior 1981; Matthess 1985).

Groundwater flows in permeable geologic formations known as aquifers. They are subdivided into porous aquifers, fractured aquifers and karstic aquifers. In porous aquifers, such as sands and gravels, groundwater flows through a complex network of interstices. The flow velocity ranges from 1 $m \cdot d^{-1}$ to a few metres per day. In fractured rocks water movement is through fractures, fissures and cracks. In karstic rocks (e.g. limestones and dolomites), the fractures are enlarged by dissolution; flow ranges from 1 $m \cdot d^{-1}$ to up to tens or hundreds of metres per day. The velocity of flow through different layers of aquifers and the dimensions of the aquifer will affect the residence time of groundwater (Matthess 1985).

The groundwater system is subdivided into saturated and unsaturated zones. In the saturated zone below the water table, the voids of the geologic formations are filled with water; its movement is primarily controlled by gravity. In the unsaturated zone, the voids are filled partly by air and partly by water. A portion of this water is bound to the surface of solid matter by adhesive forces and another portion is held by surface tension and moves by capillary action. The thickness of the unsaturated zone depends on the climate and the topography. In lowlands and in humid climates, for example, the depth may be zero or only a few centimetres; in arid zones or mountain areas, the thickness may range up to hundreds of metres (Matthess 1985).

The flow of water through the unsaturated zone is primarily vertically downward from the surface. Six hydraulic and mass transport properties affect the movement of water and the solutes it contains:

1. The hydraulic conductivity (a measure of the permeability of the media) of the soil together with the hydraulic gradient

determine the rate of movement of water (FAO 1979; Todd 1980). Hydraulic conductivity is strongly affected by soil properties such as pore size, tortuosity, the continuity of the pores and water content. In saturated soils (well-aggregated or of coarse texture) the pores tend to be continuous and the soil will have a high hydraulic conductivity. If the soil is unsaturated, the hydraulic conductivity decreases with decreases in water content.

2. The moisture content of a soil indicates the relative volume of the soil occupied by water. When the soil is saturated, water occupies all the voids of the soil and the moisture content equals the porosity.
3. The amount of active pore space versus the amount of inactive space influences the relative degree of movement. Soils with large pores readily transmit water, while smaller and isolated pores admit water by molecular diffusion.
4. The degree of soil heterogeneity affects the pore size distribution and also causes variations in the moisture profile and hydraulic conductivity, which in turn affects water movement.
5. Boundary conditions between the unsaturated and saturated zones will influence the upward or downward movement of water at any given time. In humid areas, for example, beyond the first few centimetres of soil depth, the main direction of flow is downward. In arid regions, during high periods of evapotranspiration, movement will tend to be upward (FAO 1979).
6. In unsaturated soils, there is initially a definite boundary between the resident and displacing solutions. A transition zone soon develops where the solute concentration ranges from 0 to the initial concentration of the solution. The boundary between the two solutions becomes more diffuse with time. This phenomenon is known as hydrodynamic diffusion of solutes (Freeze and Cherry 1979; FAO 1979; Neely and Blau 1985a).

In the saturated zone, the movement of water is affected by many of the same factors that affect flow in the aerated zone. Variations in hydraulic conductivity with time occur because of physical, chemical and biological factors affecting the flow characteristics of water. These include: (1) the concentration and composition of solutes in soil solution; (2) temperature; (3) changes in soil structure and bulk density; (4) air entrapment; and (5) microbial activity (Neely and Blau 1985a).

The quality of groundwater is determined by environmental factors such as geology; soil surface cover; seasonal fluctuation of recharge and discharge rates; and many of the factors affecting flow (Freeze and Cherry 1979; Matthess 1985). The velocity of groundwater flow is important when it is compared to the duration of chemical and biological processes. If the kinetics driving toward chemical equilibrium are much faster than the rate of flow through the system, variations in the flow velocity will have no effect on the hydrochemistry. If, however, the kinetics are slow compared to flow velocity, residence time in the system becomes important (Schwartz and Domenico 1983).

Gas transport in the saturated and unsaturated zones occurs by diffusion. In the saturated zone it is coupled with flow dispersion and in the unsaturated zone it is affected by temperature and atmospheric pressure. The balance between the rate of oxygen replenishment and the rate of oxygen consumption determines whether anaerobic or aerobic conditions will exist in the groundwater (Matthess 1985).

Processes such as dissolution-precipitation, oxidation-reduction, complexation and sorption further affect the quality of groundwaters. Dissolution processes will affect the concentrations of dissolved solids depending on the abundance and the solubility of the constituent substances, the solid-water interface and contact time. Oxidation-reduction conditions in groundwaters depend on the breakdown of organic substances, which is the primary source of free oxygen consumption, and the oxidation of reduced inorganic substances (e.g. Fe^{2+}, Mn^{2+}, S and NH_4^+). In the aquifer, zones of sequential utilization of oxidized species (e.g. O_2, NO_3) may develop where reduced dissolved organic carbon exceeds concentrations of dissolved oxygen. Precipitation, complexation and sorption reactions will depend on the local conditions through which the groundwaters flow (Freeze and Cherry 1979; Matthess 1985).

Groundwater may become contaminated as a result of leakage from septic tanks, sewage effluent spreading, garbage dumps and industrial waste dumps. Pollutant concentrations in groundwater are modified over time and distance travelled and by processes such as filtration, sorption, ion exchange, precipitation, microbiological decomposition and dilution. The rate of pollution attenuation depends on the type of pollution and the local hydrogeologic conditions (Todd 1980). An important aspect of groundwater pollution is the fact that it may become a long-term concern because of slow dissolution and exchange reactions, and because of slow flushing time (Blair 1974).

IV.3 LOCAL ENVIRONMENTAL CONDITIONS

IV.3.1 Dissolved Oxygen

The oxygen dissolved in surface waters is largely derived from the atmosphere and from the photosynthetic activity of algae and higher aquatic plants. In the surface waters of productive lakes, photosynthesis may produce supersaturation by day, and respiration may result in a concentration well below saturation by night (Macan 1974). Oxygen is only moderately soluble in water. Concentrations of dissolved oxygen will vary daily and seasonally and depend on the species of phytoplankton present, light penetration, nutrient availability, temperature, salinity, water movement, partial pressure of atmospheric oxygen in contact with the water, thickness of the surface film and biodepletion rates (by aquatic organisms and oxidation and decomposition processes) (Hart 1974; Mullins 1977; McNeely *et al.* 1979).

Oxygen is essential for aerobic respiration. Rates of oxygen consumption differ among organisms, depending on factors such as species, age, size, metabolic characteristics and activity. Decreased concentrations of dissolved oxygen will affect different species in various ways, from physiological impairment to death by asphyxiation. Some organisms exhibit avoidance behaviour when exposed to low concentrations of dissolved oxygen, whereas others are adapted to these conditions (Connell and Miller 1984).

Thermal stratification has important implications for concentrations of dissolved oxygen in water. It can lead to isolation of bottom waters. In the hypolimnion, the concentration of dissolved oxygen can be decreased by oxidation of inorganic wastes and nutrients and by processes that consume dissolved, suspended or precipitated organic matter (Hart 1974; McNeely *et al.* 1979). The rate and extent of decomposition depend on the amount and the type of matter available and the amount and type of bacteria present. If these processes exceed oxygen supply these waters will become anaerobic (Mullins 1977). In temperate lakes, vertical stratification usually follows a seasonal pattern. A corresponding seasonal pattern of dissolved oxygen variation will usually also develop.

Bacterial respiration is most intense at the sediment-water interface (Wetzel 1975). Dissolved oxygen concentrations in the sediment are affected by microbial metabolism; mixing with oxygenated water; and the chemical exchanges between the sediment and water (Wetzel 1975; Golterman 1975). Under anaerobic conditions, the reduced products from the various degradation processes systematically alter local water conditions of bottom waters (e.g. lower pH and redox conditions). This results in a reduction of the oxidation states of metal ions, which markedly affects the solubility of many metals, particularly those usually precipitating as hydroxides (Wetzel 1975; Mullins 1977). Aquatic organisms may, therefore, be affected both directly, because of decreased dissolved oxygen concentrations, and indirectly, by toxic effects resulting from chemical changes in localized areas produced by decreased concentrations of dissolved oxygen (Connell and Miller 1984).

In groundwaters, the water from rain or snow usually enters the subsurface flow system with a high redox potential because of its exposure to atmospheric oxygen. As it flows through the organically rich layers of the soil zone, much of the dissolved oxygen is removed by the oxidation of organic matter. In general:

1. in recharge areas with sandy or gravelly soils, shallow groundwater usually contains detectable dissolved oxygen (concentrations greater than 0.1 $mg \cdot L^{-1}$);
2. in recharge areas of silt or clay soils, shallow groundwater usually contains no detectable dissolved oxygen;
3. in areas with little or no soil overlying permeable fractured rock, dissolved oxygen at detectable levels persists deep into the flow system (Freeze and Cherry 1979).

IV.3.2 Dissolved and Particulate Matter

Dissolved and particulate matter is operationally separated into material that passes through a 0.45-μm pore-size filter, which is usually considered dissolved, and that which does not, which is designated as particulate (Drever 1982). Each of these classes of matter consists of both organic (e.g. proteins, fats, carbohydrates and related compounds and breakdown products; living organisms; dead organisms; detritus; humic and fulvic acids; colloidal substances) and inorganic (e.g. suspended minerals, rock particles, clays) material (Golterman 1975; Pagenkopf 1978; Drever 1982).

IV.3.2.1 Dissolved Matter

Dissolved organic and inorganic matter exerts a major influence on the binding of metals and other cations and on productivity (i.e. availability of and capacity for assimilation of micronutrients) (Wetzel 1975).

Complex formation involves combinations of cations (e.g. metal ions) with molecules or anions containing free pairs of electrons (ligands) (Stumm and Morgan 1970; Wetzel 1975). Simple inorganic ligands include OH^-, Cl^-, SO_4^{2-} and carbonate species. Complexation of trace metals by organic ligands in water (e.g. ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), humic and fulvic acids) enhances the total soluble metal concentration. Certain metals are preferentially complexed and competition exists among metals for complexing material, particularly organic matter, in water (Pagenkopf 1978). The extent to which metallic ions are chelated to organic matter is a function of the bonding characteristics of the organic compounds, the ratio of chelator to metal ions, the stability constants of chelates for different ions as well as temperature, hydrogen ion concentration and the concentration and ionic strength for various anions (Wetzel 1975). Complexation by dissolved matter may result in unexpectedly high total concentrations of metals in water, which may be more or less biologically available, depending upon local conditions (Drever 1982).

IV.3.2.2 Particulate Matter

Suspended particulate matter affects water clarity and light penetration, temperature, the dissolved constituents of surface water, the adsorption of toxic substances and the composition, distribution and rate of sedimentation of matter (U.S. EPA 1973).

Suspended particles may inhibit light penetration, thus greater absorption of solar energy occurs near the surface. The warmer surface water (1) will decrease density, which tends to stabilize the water column and slows or prevents vertical mixing; and (2) may reduce oxygen transfer from the air to the water. These two processes will reduce the downward rate of oxygen transfer to varying degrees in still or slow-moving water (U.S. EPA 1973).

The transportation and distribution of particles depend primarily on the transport rate of water and the transport of the particles relative to the movement of water. Dissolved metals and nutrients are transported with water movements; particulate matter, however, has a greater specific gravity than water, and transport will depend on particle size, gravity and water movement (Pagenkopf 1978).

Suspended particles have high surface areas and manifest a variety of surface effects (Connell and Miller 1984). The physical and chemical properties of these particles (e.g. distribution, sign and intensity of surface electrical charge) are important in evaluating their behaviour toward solutes in water (Hem 1985).

Cations, anions and organic compounds may be surface-adsorbed onto particulates and strongly held (Connell and Miller 1984). The fractures of inorganic particles hydrate in contact with water and adsorbed water molecules may dissociate. The release of H^+ results in a negatively charged surface, whereas the release of OH^- results in a positively charged surface. These surface charges provide the means for electrostatic-mediated sorption or complex formation. Organic substances may also sorb onto the surface of inorganic material and alter the properties of that surface (Pagenkopf 1978).

Adsorption rates are rapid; generally 50% of maximum adsorption occurs within a few minutes and maximum adsorption occurs after 30 min. Desorption rates are much slower. Both rates depend on the chemical properties of the metal and the nature of the adsorbing surface (Pagenkopf 1978). These processes are influenced by the concentration and ionic strength of the various anions and the bonding characteristics of the particles. They are also affected by local physical and chemical conditions (Stumm and Morgan 1970; Wetzel 1975).

pH strongly influences the adsorption of metal ions onto solid surfaces. The increased uptake of metal ions occurs over a narrow pH range, which often coincides with the pH range in which much of the dissolved metal hydrolyzes. A net surface charge reversal may result in this pH range if the ratio of metal ion concentration to available surface area is large. Because the pH of most natural waters ranges between 6.5 and 8.5, metal ions which hydrolyze at pH values below 8.5 will be preferentially adsorbed. For example, the changes in solubility and availability of iron and copper, as a result of complexation with certain organic molecules, are well documented (Wetzel 1975; Sprague 1985).

Colloid particles play an important role in sorption and binding processes. Metal – clay colloid ion exchange and metal sorption onto hydrous oxides and humic acid – clay colloids are two processes that play a major role in determining metal ion concentrations in water. Clays are characterized by large surface areas, cation-exchange capacities, high negative surface charges and small particle size. The actual process by which clay minerals concentrate substances is not well understood; however, studies show that it depends on factors such as the valence and concentration of the constituent, the type of clay, the pH of the water and the nature and concentration of competing substrates (Forstner and Wittmann 1979). Jenne (1976) suggests that the major role of clay minerals in terms of metal concentrators is to act as substrates for the precipitation and flocculation of organic matter and hydrous iron and manganese oxides. The clays are covered with material that, rather than the clay itself, attracts trace metals. Within a pH range of 6.5-8.5, the surface of clay particles is usually negative to which cations (e.g. H^+, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}) sorb. Sorption is not permanent and cations are constantly being exchanged by other cations (Babich and Stotzky 1983). Much of the iron in natural waters, for example, is present as suspensions of ferric hydroxide ($Fe(OH)_3$). Under specific conditions, a very finely divided $Fe(OH)_3$ precipitate, which has the properties of a colloid, may form. These particles usually have a positive surface charge, and may attract ions in solution, negatively charged clay particles, organic colloids, etc. The resulting uncharged aggregates join to form a settling precipitate. Metals, such as copper ions, may be adsorbed by and coprecipitated with the $Fe(OH)_3$ precipitate (Wetzel 1975).

IV.3.2.3 Bed Sediments

The effects of bed sediments on water quality vary depending on local conditions and the chemical nature of the sediments. Sorption mechanisms, redox and the activity of bacteria, fungi, periphyton, plankton and invertebrates influence exchanges across the sediment-water interface. The rates of these processes are a function of local diffusion coefficients and the environmental conditions affecting chemical reactions (Wetzel 1975).

Once sediment is deposited, the organic matter within it provides a substrate for bacterial growth and contributes to low redox (Golterman 1975). Sediments are a key area for biogeochemical transformations. The rate of oxygen depletion from sediment can be high, and results from microbial activity (most intense at the sediment-water interface), from the chemical demand resulting from diffusion and from the reduced forms of inorganic elements (e.g. Fe^{2+}, Mn^{2+}) released from biotic decomposition in sediment (Wetzel 1975).

When a metal reaches the sediment bed it may be recycled via physical (e.g. water turbulence) and chemical (e.g. increased salinity, lowered pH, leaching by organic acids) processes and released back into the water column (Golterman *et al.* 1983). Under changing hydrologic conditions (e.g. spring runoff, heavy storms) a localized pollution problem might become widespread and cause significant environmental impact (Horowitz 1985).

A major concern of microbial activity relates to the conversion of inorganic metal compounds to organic molecules as a result of enzyme-catalyzed oxidative and reductive processes. The formation of methylated compounds of arsenic, lead, mercury, selenium and tin, for example, provides a means of release of toxic substances to the environment. The rate of methylation is closely related to microbial activity. Methylation appears to take place near the sediment-water interface and on particulates in suspension (Golterman *et al.* 1983).

Many concerns relate to the accumulation of heavy metals (Hg, Cd, Pb, Cu, As) in the food web. Because the greater proportion of the metals is associated with silt and clays, accumulation in the food chain begins with the filter-feeding zooplankton (Golterman 1975).

The flux of nutrients out of sediments is important in determining the trophic state (biological productivity and oxygen distribution) in a water body (Drever 1982). The exchange of phosphorus, for example, between the sediment and water is important to the overall availability of phosphorus in natural waters. The main factors controlling the process are the ability of the sediments to retain phosphorus, the local conditions of the overlying waters (redox, pH and concentrations of other substances) and the microorganisms within the sediment that modify exchange equilibria and affect phosphorus transport (Wetzel 1975; Golterman 1975). A significant fraction of phosphorus is adsorbed onto ferric hydroxide and oxides which, at low redox, dissolve and release phosphorus. Dissolved phosphorus concentrations are usually at a minimum at pH 5-7 (Connell and Miller 1984).

IV.3.3 Flow and Volume

The movement of materials in water follows diffusion and dispersal patterns that characterize each water body or water mass within it (Golterman *et al.* 1983). Dissolved substances move at the velocity of water, whereas colloidal and particulate matter undergo additional transport processes, such as sedimentation or resuspension.

The movement of materials in water depends on advection and dispersion. Advection refers to the movement of dissolved or fine particulate material at the current velocity in any of three directions (longitudinal, lateral or transverse, and vertical). Dispersion refers to the process by which these substances are mixed within the water column and can also occur in three directions. The transport of dissolved substances is principally by advection in streams and rivers, and predominantly by dispersion in lakes. The mass flux of dissolved substances will be from areas of high concentration to areas of low concentration (Neely and Blau 1985b).

The effect of flow on many physical, chemical and biological parameters is used in predictive mathematical models for estimating water quality. Many rivers show an annual mean pattern of flow which is related to seasonality. Hydrographs provide important information on the degree of variation in flows and the identification of critical periods. Streamflow is an important measurement for the quantitative analysis of pollution problems because it affects the dilution properties of a river. Periods of high flow, for example, enhance the natural aeration processes by increased turbulence. During low flow, dilution is reduced and sediments settle on the river bottom together with any absorbed pollutants. In large rivers with comparatively shallow water and low water velocities natural mixing processes may be reduced and heterogeneity in chemical composition may be observed. In addition, parallel currents of different chemical composition may form downstream of a tributary joining a river or the inflow of waste into a river (IHP 1982). Long-term changes in the concentration of surface waters may result from long rainfall or runoff cycles; seasonal variations in flow may be expected from changing rates of runoff, evaporation and transpiration. Daily and hourly changes may occur as a result of flash floods or human regulation of flow. Water quality measurements are therefore changeable and susceptible to location bias and temporal variations (U.S. General Accounting Office 1981).

Volume will affect chemical concentrations (dilution effect) and physical processes such as lateral and longitudinal dispersion, mixing, suspension and sedimentation (Golterman *et al.* 1983). In rivers, changes in the volume of base flow with time will change the relative importance of other sources of input, such as groundwater and runoff (Hem 1985). Severe variations in the volume will affect channel morphology and substrate composition (chemical conditions and physical processes). The impact on the lake conditions by single tributaries depends upon their inflow rate relative to the water budget of the lake and to the degree of mixing of the incoming water with the lake water. Vertical mixing in lakes differs from that in rivers, as chemical and thermal stratification serves to limit this type of mixing (Neely and Blau 1985b).

The intensity of variations in the current determines the occurrence and distribution of many aquatic organisms largely through its effect on feeding and respiration. Some species depend on the current to bring food and to supply their oxygen requirements (Macan 1974). Shifts in current velocity may also affect the streambed, disturb habitats for macroinvertebrates and disrupt productivity, diversity and species composition of aquatic communities.

IV.3.4 Hardness

The hardness of a water body is regulated largely by the levels of calcium and magnesium salts. The presence of other constituents, such as iron, manganese and aluminum, may contribute to hardness, but are not usually present in appreciable concentrations (Wetzel 1975). Hardness is usually expressed as an equivalent of calcium carbonate ($CaCO_3$), and varies according to local conditions. Hardness is used as an indication of water type, buffering capacity and productivity. For example, in the presence of carbonate bedrock, waters are usually "hard" and tend towards large concentrations of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) and increased pH (McNeely *et al.* 1979; Borgmann 1983).

As the calcium ion concentration decreases in a water body, so does its buffering capacity. Water bodies with low concentrations of calcium are more susceptible to an increase in hydrogen ion concentration from an acid input and subsequent changes in the physical and chemical properties of the system (Borgmann 1983; O'Donnel *et al.* 1985).

Some evidence suggests that hard water mediates the toxicity of many metals to aquatic life, because of carbonate complexation and calcium antagonism (U.S. EPA 1973). The complex and equivocal interrelationship of hardness, pH and alkalinity is documented with studies on copper toxicity. It is reported that the ionic form of the metal is very toxic, as are ionized hydroxides of copper, but possibly not its un-ionized carbonates. If hardness is kept constant and alkalinity changed, the toxicity changes. Furthermore, for the same hardness, the toxic forms of the metal are greater at high than at low pH (Sprague 1985).

IV.3.5 Metals

Metals from Groups I and II of the periodic table as well as trace amounts of other metals are found in natural water (Stumm and Morgan 1970). The speciation and bioavailability of trace metals in water are controlled by physical and chemical interactions and equilibria. These interactions are affected by many factors, including pH, redox, temperature, hardness, CO_2 concentrations, the type and concentration of available ligands and chelating agents and type and concentrations of metal ions (Mullins 1977; Connell and Miller 1984; Westman 1985). Concerns over metals relate to their toxicity and bioavailability, particularly for uncomplexed ions, the potential for bioaccumulation and hazards to human health.

Because metals do not degrade, they are transferred or stored in the aquatic medium and should be considered as "available" under the appropriate conditions (Mullins 1977; Pagenkopf 1978). Lead, for example, is strongly adsorbed to particles and can be removed from the water column and concentrated in sediments. Cadmium, which complexes with organics, is likely to remain in water (Laxen 1983). The spatial distribution of metals in water is a function of water movement (e.g. water mass, currents, mixing phenomena), chemical form and solubility. For metals associated with colloids and particulate matter in suspension, transportation is further regulated by particle size, shape and density and the turbulence of the aquatic medium (Mullins 1977; Pagenkopf 1978).

Sediments and surface film are two important sites of metal enrichment. Concentrations of metals orders of magnitude above those dissolved in water have been documented. Enrichment factors for metals, varying from 5.8 for particulate lead to 50 for particulate nickel, have been reported in the surface film (top 100-150 μm) (Mullins 1977). The transfer of metals between sediments and the water above them is a complex process and depends on many factors (e.g. oxygen concentration, pH, concentration of heavy metals and organic and inorganic ligands). Some of the individual processes involved in this transfer are dissolution, ion exchange, complexation, sorption, precipitation and coprecipitation (Jenne and Luoma 1977).

Metals may exist in the soluble form as simple or complex free metal ions, ion pairs, coordination compounds or unionized organometallic chelates or complexes. Complexes may be formed with anionic species (e.g. OH^-, Cl^-, SO_4^{2-}, HCO_3^-, organic acids and amino acids); associations with colloid and particulate material include clays, organic matter, hydrous iron and manganese oxides. The degree of metal speciation is regulated by the pH of water, the stability of the hydrolysis products and the tendency of the metal ion to form complexes with other organic and inorganic ligands (Pagenkopf 1978; Connell and Miller 1984).

Metals will complex with inorganic and organic ligands. The dominant inorganic complexing ligands include Cl^-, SO_4^{2-}, HCO_3^-, F^-, sulphide, and phosphate species. Metals may bond to natural and synthetic organics via (1) carbon atom donor organometallic compounds; (2) carboxylic groups producing organic acid salts; (3) coordination complexes with O, N, S and P; and (4) π-electron donating groups (Connell and Miller 1984). Studies show that complexing ligands are an important factor in determining the speciation and adsorption processes of trace metals on hydrous oxides in solution (Stumm and Morgan 1970; Pagenkopf 1978).

Metal ions may be removed from the water column by adsorption, precipitation and coprecipitation processes. The rates of these processes, however, are not easily defined. Adsorption by solid surfaces is pH-dependent and increases as the metal ion hydrolyzes. Because the pH lies between 6.5 and 8.5 for most natural waters, metal ions hydrolyzing at pH levels lower than 8.5 will be preferentially adsorbed (Pagenkopf 1978).

Oxidation-reduction conditions are important in metal speciation because they directly affect the oxidation state of the metal ion (Connell and Miller 1984). The hydroxides and oxides of Fe and Mn, for example, constitute an important sink for trace metals (e.g. Co, Ni, Cu and Zn). In reducing environments, Fe(III) will be reduced to Fe(II), and Mn(IV) will be reduced to Mn(II). The net effect of lower oxidation states for these two metals is dissolution and desorption of trace metals (Stumm and Morgan 1970; Pagenkopf 1978).

Three major microbial processes affect the transport and transformation of metals in sediments: (1) degradation of organic matter by microorganisms, resulting in lower-molecular-weight components which are more capable of complexing dissolved metals; (2) inorganic compounds which may be transformed into organometallic forms by means of oxidative and reductive processes (e.g. methylation of Hg, As, Pb, Se and Sn); and (3) changes to the physical and chemical properties of the environment and the species of metals by metabolic activities (Connell and Miller 1984).

Chemical transformations are seldom simple one-step reactions. Usually one chemical species will predominate at any one moment, but all metal species can be present to some degree (Laxen 1983). Multivalent metal ions, for example, are known to form soluble or insoluble complexes with substances containing carboxyl, hydroxyl, sulphate and phosphate groups (Stumm and Morgan 1970). Although it is theoretically possible to determine an equilibrium constant for the formation of metal complexes, it is difficult to determine in advance which ions are most stable. The study of stability constant data will help to indicate which complex ion will prevail in the speciation of an individual metal ion (Pagenkopf 1978).

Determination of the bioavailability of the metal requires information on the physical form and chemical speciation of the metal and the interactions among the various forms (Laxen 1983). Studies show, for example, that uncomplexed ions, such as Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, are usually more readily available to aquatic biota than are complexed forms (Leland and Kuwabara 1985). The effects of metal exposure on physiological processes are complex and variable (Connell and Miller 1984). Furthermore, metals usually occur in combination in nature, and, therefore, the overall toxicity to aquatic biota may change (Mullins 1977).

Implicit in studies of correlations between bulk sediment concentrations of metals and bioavailability is the assumption that the solubilizing strength of the extracting solution used for analysis of the sediment-bound metal is similar to that which the organism exerts. If it is not, then the bioavailability of the metal may be over- or underestimated because of the heterogeneous nature of the metal-sediment interaction (O'Donnel *et al.* 1985).

Although separate guidelines for the different forms of many metals are needed, problems with the measurement of these different forms and the relative toxicities of the different metal species complicate the formulation of chemical species-specific guidelines for most metals. Usually total concentrations of metals are reported as a protective measure (Robertson 1985).

IV.3.6 Nutrients

Nutrients play a major role in the synthesis of living material. Some elements are needed only in trace amounts. Others, such as carbon, oxygen, hydrogen, sulphur, nitrogen and phosphorus, are required in larger quantities. Eutrophication refers to the addition of nutrients to bodies of water and the effects of these nutrients on water quality and on aquatic life. Water bodies with little flushing, such as lakes and reservoirs, are susceptible to eutrophication through nutrient enrichment over geological time. Nutrient enrichment and eutrophication may be greatly accelerated by human activities.

Variations in the concentration and distribution of nutrients depend on many factors, including seasonal variations in local conditions and the biological activity of the area (Mullins 1977). In general, to assess the effects of nutrient enrichment on a water body, the identification of the limiting nutrients and their relationship to plant growth must be determined (Thurston *et al.* 1979).

The availability of nitrogen and phosphorus to plants is governed by a complex series of biologically mediated reactions. In a photosynthetic zone, phosphate and nitrate uptake from water for algal growth occurs at a ratio approaching 1:16.

These nutrients are released to the water, at the same ratio, upon mineralization of settling algae in deeper water (Stumm and Morgan 1970).

The nitrogen cycle is one of the major biogeochemical cycles. The principal aspects of the cycle are fixation of molecular nitrogen, ammonification of organically bound nitrogen, nitrification and denitrification (Verschueren 1983). The photosynthetic activity of aquatic plants plays a major role in the conversion of inorganic to organic nitrogen.

Molecular nitrogen undergoes a complex series of interactions in the nitrogen cycle and is eventually converted to ammonia (NH_3), nitrite ion (NO_2^-) and nitrate ion (NO_3^-). Both ammonia and nitrate are readily bioavailable and enter into most growth processes.

Discharges of various forms of nitrogen into aquatic systems (e.g. municipal sewage) alter the natural nitrogen cycle because of large inputs of ammonia. Ammonia is the main decomposition product of plant and animal proteins. It is readily oxidized to nitrite and nitrate in the presence of sufficient oxygen (nitrification). The process depends on pH, dissolved oxygen, temperature and bacterial populations, and, depending on the circumstances, may decrease concentrations of dissolved oxygen.

Ammonia is readily bioavailable as a nutrient for plant uptake, and, therefore, may contribute greatly to increased productivity. As plant cells die and fall to the bed sediment, oxygen demand increases and plant materials build up a pool of mineralizable nutrients. Unlike other cycles, such as the phosphorus cycle, very little nitrogen is lost from the system by inorganic precipitation.

Bacteria play a major role in the conversion of inorganic nitrogen to a biologically available form. Microbial degradation of organic and inorganic matter in the sediments results in the formation of carbon dioxide, orthophosphate, ammonia, nitrite and nitrate (under different conditions) and the consumption of dissolved oxygen. Excessive inputs of nitrogen from agricultural runoff and effluent discharges, however, can disrupt physical and chemical conditions, change microbial communities and impede bacterial action.

In bottom waters under anaerobic conditions, organic nitrogen is converted into ionized (NH_4^+) and un-ionized (NH_3) ammonia (Golterman 1975; Russo 1985). Un-ionized ammonia is toxic to fish at relatively low concentrations; however, it is in equilibrium with the less toxic NH_4^+ ion (Lack 1984). The concentration of each form depends on pH and temperature. Tabulations of percentages of NH_3 in solution of total ammonia within certain temperature and pH ranges are available (Thurston *et al.* 1979). Factors such as pH, dissolved oxygen, temperature, calcium concentrations, alkalinity and presence of other pollutants also influence the toxic effects of ammonia. The action of some mixtures of ammonia and various toxicants is summarized below (Russo 1985):

Combinations	*Action*
ammonia and copper	synergism
ammonia and zinc	synergism
ammonia and nitrate	additive effects (except at low ratios)
ammonia and hydrogen cyanide	synergism
ammonia, zinc, phenol	synergism

Because nitrites are rapidly oxidized to nitrate, only trace levels are usually found in surface waters. The relationship between nitrite toxicity and pH indicates that beyond pH 6.4-9.0, the toxicity of total nitrite decreases as pH increases. Some anions, such as Cl^-, Br^-, SO_4^{2-}, PO_4^{3-} and NO_3^-, moderate nitrite toxicity to varying degrees (Russo 1985).

Phosphate is released into natural waters by the weathering of rocks. Depending on the pH, orthophosphate may exist in any of three forms (i.e. H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}); the predominant forms at pH 6-8 are $H_2PO_4^-$ (10%) and HPO_4^{2-} (90%). The latter is the principal nutrient form (Reid and Wood 1976).

Orthophosphates are bioavailable. Once assimilated, they are converted to organic phosphorus and into condensed phosphates. Upon death of an organism, the condensed phosphates are released into the water. They are not available for biological uptake, however, until they are hydrolyzed into orthophosphates by bacteria.

The availability of phosphorus to biota depends on the uptake and release rates by biota, chemical speciation (e.g. organic or inorganic bound phosphorus) and the relative abundance and residence time of the dissolved phosphorus fraction.

Phosphates will readily complex with cations available in the water (e.g. Fe, Al, Ca) to form insoluble complexes, chelates and salts (Stumm and Morgan 1970). The formation and dissolution of these compounds are major components of the phosphorus cycle and are a function of pH, the concentration of phosphates, metal ions and ligands, the solubility of various metal-phosphate compounds, the redox potential and biotic activities (bacteria, fungi, plankton, invertebrates) (Wetzel 1975; Thurston *et al.* 1979). These associations will remove phosphate from the system and reduce the concentration of some metals by precipitation of the metals as phosphate-containing salts (Babich and Stotzky 1983).

Nutrient enrichment and eutrophication result in many changes in aquatic populations and communities. The species composition of phytoplankton may shift to those more tolerant of nutrient-rich conditions. Under these circumstances, blue-green algae may dominate. Increases in algal productivity lead to increased decomposition of organic matter and a corresponding utilization of dissolved oxygen. Low concentrations of dissolved oxygen in the hypolimnion of lakes often occur in the summer because of these decomposition processes and the effect of stratification on exchanges with atmospheric oxygen (IJC 1978). Population diversity and density for fish and benthic organisms will be affected, and, if conditions persist for long periods, different biotic communities may become established.

IV.3.7 pH, Alkalinity and Acidity

Hydrogen ion (H^+) and hydroxide ion (OH^-) concentrations are important properties of aquatic systems because they effectively influence the physical, chemical and biological processes occurring in water.

The pH of water approximates the activity of free hydrogen ions in water. It is defined as the negative logarithm of the hydrogen ion concentration. The pH scale indicates the balance between acids and bases in water. It is important in all chemical reactions associated with the formation, alteration and dissolution of minerals (McNeely *et al.* 1979; Stumm and Morgan 1981).

The major influence on hydrogen ions and the parameters affecting alkalinity and acidity is the geology of the watershed. Dissolution processes take place because of the thermodynamic instability of many minerals in the presence of water and the atmosphere. Ca^+, HCO_3^-, H^+ and Mg^{2+} may be controlled by the dissolution of carbonate rock. The sources of Na^+, K^+, H_4SiO_4 and possibly Ca^{2+} and Mg^{2+} are the silicate minerals that make up much of the rock in contact with underground waters and streams. Dissolution processes may be altered by formation of complexes or changes in oxidation states which, in turn, influence the concentration of acids, bases and H^+ ions (Westall and Stumm 1980; Stumm and Morgan 1981).

Biological processes (e.g. photosynthesis and respiration) as well as turbulence and aeration influence the pH by varying the concentrations of dissolved carbon dioxide. The pH is likely to increase during photosynthesis and decrease during respiration processes (McNeely *et al.* 1979).

The pH of water affects transformation processes among the various forms of nutrients and metals, and influences the toxicity of pollutants consisting of acids and bases because of the effects of ionization on these compounds. When in the molecular form, these pollutants usually penetrate the membranes of fish and other aquatic life more easily (Sprague 1985).

The pH plays a major role in the chemical speciation of many metals, their water solubility and their bioavailability. The stability of many metal complexes in water is reflected in low or reduced dissociation rates. Although some rates are so low that it may take years for the complex to dissociate, the process can often be accelerated by the interactions of competing ligands or by increased availability of hydrogen ions (Pagenkopf 1978).

At high pH, many metals form hydroxides or carbonates which are relatively insoluble and usually precipitate. Metallic hydroxides of iron and manganese, for example, act as scavengers for many heavy metals. Decreases in pH will change the surface charges and attractive forces of these hydroxides and result in the release of sorbed metal ions (Faust and Aly 1981; Eichenberger and Chen 1982). This is because some metal ions hydrolyze at low pH; the hydrogen ion thus produced will interfere with adsorption and ion exchange by competing for active sites (Pagenkopf 1978; Eichenberger and Chen 1982). Because the adsorption process is reversible and depends on pH, it raises concerns about the effects of increased acidity of receiving waters on the release of metals from sediments (Faust and Aly 1981; Eichenberger and Chen 1982).

Hydrogen ion regulation in water is provided by many types of buffer systems. Alkalinity and acidity are capacity factors that represent the acid- and base-neutralizing capacities, respectively, of the aquatic environment. Alkalinity and acidity provide a measure for estimating the maximum capacity of natural water to neutralize acidic and alkaline wastes without causing extreme disturbance of biological activities in the water (Stumm and Morgan 1981).

Total alkalinity is, in general, the sum of all the components in the water system that act to buffer the water against changes in pH (e.g. bicarbonate and carbonate from the carbonate system, as well as hydroxides, sulphides, silicates and phosphates). The species composition of alkalinity depends on pH, mineral composition, temperature and ionic strength (U.S. EPA 1973). There is often a good correlation between specific conductance and the alkalinity of natural waters. This relationship is significant when Ca^{2+} and HCO_3^- ions constitute the major portion of the ions. Deviations from this relationship would suggest that other ions predominate (Kramer 1982).

The major buffering system in natural waters is the carbonate system. The precipitation of insoluble carbonates and hydroxides and the loss of carbon dioxide are two processes that alter alkalinity. The first process results in a lowering of the total alkalinity, whereas the latter will alter the distribution of the chemical species but not change the total alkalinity (U.S. EPA 1973; Pagenkopf 1978). The carbonate system not only neutralizes acids and bases, resulting in reduced fluctuations in pH, but also forms a reservoir of carbon for photosynthesis. The productivity of waters is, therefore, closely related to the carbonate buffering system.

IV.3.8 Temperature

Water temperature varies with geographical location, seasonality, diurnal variations, characteristics of the water body (flow, depth, etc.) and anthropogenic effects (McNeely *et al.* 1979; Sprague 1985).

The thermal and circulation characteristics of lakes result from the effect of seasonal variations in temperature. The heating of surface waters creates a thermal discontinuity within a stable water body and divides the water into thermal strata, each with its own physical, biological and chemical characteristics. The epilimnion (heated and mixed upper-layer water) and hypolimnion (cold and relatively stagnant bottom water) are separated by the thermocline. The reverse process, destratification, results from the breakdown of thermal stratification. Cooled surface water will sink into deeper water as long as its density exceeds the density of the surrounding waters. This leads to the gradual reduction and finally the disappearance of a temperature difference throughout the water. Homothermal lake water may be fully overturned and mixed by wind action (Frevert 1985). The temperature profile for rivers and streams is generally more homogeneous, largely because turbulent streamflow assures good vertical mixing.

In groundwaters, the geothermal gradient is greater near the surface in discharge areas than it is in recharge areas. The gradient increases with increasing depth in recharge areas, and decreases with increasing depth in discharge areas. The effects of the temperature gradient are greater in high-permeability geological formations, where flow velocity is higher, than in low-permeability formations, where velocity is lower (Freeze and Cherry 1979).

Temperature plays a major role in influencing aquatic life and the physical and chemical parameters of the aquatic environment. Changes in temperature will affect solubility and chemical reaction equilibria (Mullins 1977). Increases in temperature decrease the solubility of dissolved gases (H_2, N_2, CO_2 and O_2) in water. Within a range of 0-30°C, for example, oxygen solubility decreases by approximately 50%. Viscosity, surface tension, compressibility, specific heat, ionization constants and latent heat of vaporization all decrease as the temperature increases (Houston 1982). Increases in temperature will increase thermal conductivity, vapour pressure, the solubility of salts and the rate of chemical oxidation of substances (Golterman *et al.* 1978; Westman 1985). Temperature also influences the pH because of its effect on the dissociation of acids and the solubility of CO_2. In general, a rise in temperature of 20°C will lower the pH by 0.1 pH unit (Golterman *et al.* 1978).

There is no easily defined pattern for predicting the effects of temperature on the toxicity of pollutants to aquatic organisms. For example, EIFAC (1976) reported on the complexity of the relationship between temperature and copper toxicity. There is also evidence that temperature affects the solubility and volatility of many chemicals in water (Connell and Miller 1984).

The biochemical processes of aquatic organisms governing metabolism, reproduction, growth and behaviour are very sensitive to temperature, and changes in temperature will affect the rates of these processes. Respiration rates, for example, increase with temperature, and lead to a higher rate of metabolism and excretion. Thus, the organism requires more oxygen in an environment which contains less than before, and may suffocate. The rates of metabolism and excretion would be expected to double for every 10°C increase in temperature (Q_{10} rule) (Connell and Miller 1984). Aquatic biota will differ in their tolerance to temperature changes according to factors such as species, age, acclimation temperature, dissolved oxygen, exposure to toxic substances and season (Alabaster and Lloyd 1984; Rand and Petrocelli 1985).

One cause of increased environmental temperatures in water is the use of water as a coolant in industrial processes. The discharge of warm water decreases the amount of dissolved oxygen near the discharge point. This is because warm water cannot dissolve as much oxygen as cold water and, being lighter than cold water, forms a blanketing layer on the surface. The discharge of warm water may also have more subtle effects, such as giving false temperature cues to aquatic organisms and causing inappropriate behaviour for the time of year (e.g. migration and spawning) (Duffus 1980). In groundwaters, quality may be affected by heated spent cooling water if the water contains biostimulants or other chemicals which produce adverse effects that are accelerated by increased temperature (ASCE 1972).

IV.3.9 Total Dissolved Solids

Total dissolved solids (TDS) is a general term referring to the concentration of dissolved matter in water. The principal anions include carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates. The major cations include calcium, magnesium, sodium, potassium and iron. Many of these constituents are essential to life processes, and the reader is referred to Chapter 6 for detailed information on each constituent.

The presence and abundance of TDS in a water body are largely regulated by factors such as the chemical composition of influents, surface runoff and subsurface infusion, the geochemistry of the watershed, atmospheric precipitation, anthropogenic effluents and biological and chemical processes. The concentrations and relative proportions of TDS are subject to spatial and temporal variation (Wetzel 1975).

The distribution of the major ions contributing to TDS falls into two categories. Conservative ions, such as Mg^{2+}, Na^+, K^+ and Cl^-, are subject to relatively minor fluctuations from biological utilization or biologically mediated changes in the environment. Dynamic ions, such as CO_3^{2-}, SO_4^{2-}, Ca^{2+} and inorganic carbon, are influenced by microbial metabolism (Wetzel 1975). The presence of large quantities of Ca^{2+} and HCO_3^- ions is important in determining and buffering the pH of water.

The concentration of total dissolved solids is of interest primarily because:

1. the concentration determines the electrolyte characteristic or ionic strength of the solution (the ionic strength is related to the activity coefficient and, therefore, to the solubility of solutes); and
2. the anions participate in complexation and precipitation processes with many trace metals (Mullins 1977; Pagenkopf 1978).

In natural waters, carbonates, sulphates, chlorides, phosphates and nitrates affect metal speciation by forming ionizable salts. Insoluble carbonate formation is one of the most important processes for removing metals from solution (Stumm and Morgan 1970; Pagenkopf 1978).

The composition and concentration of total dissolved solids are important in determining the variety and abundance of aquatic plants and fauna. The chemical density of the aquatic environment influences the osmotic regulation of metabolism and biotic distribution. Furthermore, dissolved solids constitute the sole source of nutritionally important ions to phytoplankton (Wetzel 1975). A major change in the quantity or composition of total dissolved solids will affect the structure and function of the local aquatic ecosystem.

IV.3.10 Turbidity

Turbidity is a measure of water clarity. It provides approximations for concentrations of suspended material, such as clay, sand, silt, finely divided organic and inorganic matter, plankton and other microorganisms in water (McNeely *et al.* 1979). It is related to seasonal factors and flow regimes, and is affected by snowmelt and rain events. Turbidity varies from one location to another depending on: hydraulic forces; vegetative cover; type of soil; and anthropogenic influences through agriculture, lumbering, mining, etc.

The primary effect of substances causing turbidity is an attenuation in light intensity with depth. Greater absorption of solar energy, therefore, occurs near the surface. The warmer surface water (1) will decrease density, which tends to stabilize the water column and slows or prevents vertical mixing; and (2) may reduce oxygen transfer from the air to the water. These two processes will reduce the downward rate of oxygen transfer to varying degrees in still or slow-moving water (U.S. EPA 1973).

Increases in turbidity and colour, in limiting light penetration, will reduce photosynthesis and will have a direct influence on the amount of biological production occurring within the body of water. These parameters can effectively limit the efficiency of sight-feeding fish and zooplankton migrations, and interfere with benthic invertebrate reproduction (Alabaster and Lloyd 1984; Connell and Miller 1984). Suspended solids will clog the filter apparatus of some immature stages of insects (e.g. caddis larvae) and fish and cause physical injury to delicate eye and gill membranes by abrasion. If the suspended material is rich in organic matter, effects may be further aggravated by changes brought on by deoxygenation (Connell and Miller 1984).

Radionuclides, organics and metals also tend to accumulate on the surface of colloids and particles. The complexing and adsorptive behaviour of colloids and particles changes as they are carried from one location to another and meet different physical and chemical conditions.

IV.4 PROCESSES AFFECTING THE CONCENTRATION OF PARAMETERS IN WATER

IV.4.1 Introduction

The fate and concentration of substances in water may be affected by the following processes: complexation; hydrolysis; ion exchange; microbial degradation; oxidation-reduction; photolysis and phototransformation; precipitation and coprecipitation; solubility; sorption; and volatilization.

These processes, in turn, can significantly affect the availability, toxicity, persistence and fate of substances in water. As with other parameters, the rate and degree to which these processes occur depend on the prevailing local environmental conditions.

IV.4.2 Complexation

The forms of metal ions in solution are important for determining chemical, biochemical and biological effects. Each metal ion has a speciation pattern that is a function of the stability of the hydrolysis products and the tendency of the metal ion to form complexes with other ligands (Connell and Miller 1984). Metal ions react with organic matter (O and N functional groups) and inorganic complexing materials (OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-) in water from both natural and pollution sources (Westall and Stumm 1980). Complexation reactions often involve sequences of soluble complex ions and insoluble phases depending on the metal and ligand concentrations and the pH. These interactions determine metal speciation in water and contribute greatly to the overall regulation of metal ion concentration in water (Pagenkopf 1978).

A coordination complex results from the combination of a metal cation with an anion containing free pairs of electrons. The cation is termed the central atom and the anion the ligand. Complexes with more than one ligand group are called chelates. Two types of metal-ligand bonds can be distinguished: ion pairs and coordination complexes (Golterman 1975).

In ion pairs, the metal and ligand retain their hydration spheres in forming a complex. The bonding is through one or more water molecules and is primarily electrostatic. Their formation depends on the ionic strength of the waters and on the properties of the particular ion. Ion pairs are particularly important in metal speciation in waters with high hardness, alkalinity and sulphate concentrations (Pagenkopf 1978).

Coordination complexes are distinguished by the ligand being immediately adjacent to the metal cation. A certain degree of electron transfer from the ligand to the metal occurs (Stumm and Morgan 1970; Westall and Stumm 1980). Some organic ligands form coordinate bonds, largely covalent, with more than one functional group (multidentate ligands or chelates). Chelates are usually more stable than simple complexes or ion pairs (Westall and Stumm 1980; Stumm and Morgan 1981).

The pH affects the degree of complex formation. At low pH, H^+ competes with the metal ions for the ligand, whereas at high pH, OH^- competes with the ligand for the coordinative positions on the metal ion. At both high and low pH, mixed hydrogen-metal and hydroxide-ligand complexes can occur. The tendency towards complex formation increases with the ionization potential of the metal and with increasing tendency for the ligand to donate electrons. In water chemistry, some of the more important complexes formed are those with the hydroxide species. With most tri- and tetravalent metal ions, the hydroxides are the only stable precipitates in the pH range of natural waters (Stumm and Morgan 1970; Pagenkopf 1978).

Redox changes will affect metal speciation in two ways: (1) by direct changes in the oxidation state of the metal ions (e.g. Fe(II) to Fe(III)); and (2) by redox changes in available and competing ligands or chelates (Connell and Miller 1984).

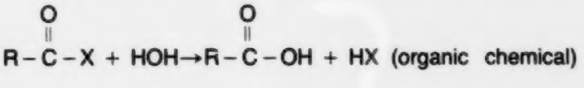
Tabulations of stability constants for the stepwise formation of complexes are available for both inorganic and organic ligands. Analysis of these constants will indicate which complex ion will prevail in the speciation of a particular metal ion, but will not indicate which complex ions are the most stable. Metals forming more stable complexes may displace other less strongly complexed metals. The stability of a complex is reflected in a low dissociation rate. The rate can be accelerated, however, with the introduction of hydrogen ions or other competing ligands (Pagenkopf 1978; Connell and Miller 1984).

The behaviour of metals is greatly affected by interactions between aqueous and solid phases. Dissolved metal complexes can be removed from water on contact with the surfaces of particulate matter and deposited to sediment beds. Enrichment and remobilization of metals in sediments depend on factors such as chemical composition, salinity, pH, redox values and local hydrodynamic conditions (Connell and Miller 1984). Metal concentrations in solution that are higher than those calculated are often explained by chelation with organic molecules. Chelation may also contribute to masking the presence of metals in water (Stumm and Morgan 1970).

IV.4.3 Hydrolysis

Hydrolysis occurs when an organic compound or metal salt reacts with water and results in the net exchange of the group X for a hydroxyl function (OH) (Connell and Miller 1984):

$RX + HOH \rightarrow ROH + HX$ (or H^+, X^-) (organic chemical)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-X + HOH \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HX \quad \text{(organic chemical)}$$

$MX + HOH \rightarrow MOH + H^+ + X^-$ (metal salt)

The importance of hydrolysis is that the reaction introduces a hydroxyl group into the parent molecule. For organic compounds, the resulting product is usually more vulnerable to further breakdown by biodegradation and photolysis. In addition, the hydroxyl group makes the compound more water-soluble, and therefore reduces the potential for bioconcentration (Neely and Blau 1985a).

Soluble hydrolysis products are important in aquatic environments where metal ions are present. The low cation concentrations and the relatively wide range of pH within which hydroxo and oxo complexes may exist can significantly alter the chemical behaviour of these metals (Eichenberger and Chen 1982).

Hydrolysis reactions may be induced by an acid (H_30^+) or a base (OH^-) catalyst (U.S. EPA 1979). The rate expressions describing hydrolysis reactions are complex; however, the processes can be described by relatively simple relationships, provided that pollutant removal rather than product formation is the focus (NRCC 1981).

The rate expression for neutral, acid- and base-catalyzed hydrolysis is (NRCC 1981):

$$-\frac{d[P]}{dt} = K_{H_3O^+}[H_3O^+][P] + K_{H_2O}[H_2O][P] + K_{OH^-}[OH^-][P]$$

where K_{H_2O}, $K_{H_3O^+}$, K_{OH^-} = second-order rate constants for neutral, acid-catalyzed and base-catalyzed reactions, respectively

[P] = concentration of the hydrolysate.

Temperature affects hydrolysis in that each rise of 10°C increases the rate of reaction two- to fourfold (NRCC 1981).

Stumm and Morgan (1970) have established two rules for the hydrolysis of cations:

1. dilution and decreasing $[H^+]$ increase the tendency of metal ions to hydrolyze; and
2. dilution decreases the fraction of polynuclear complexes in water.

Hydrolyzed products of multivalent metal ions are adsorbed more readily at the particle-water interface than are non-hydrolyzed metal ions. Several explanations have been advanced, but no proven theories are available (Stumm and Morgan 1970).

The chemical species and oxidation states of hydrolytic products can control many aspects of chemical behaviour, such as: (1) the adsorption of soluble species on particulates; (2) the likelihood of the metal species to coagulate colloid particles and to form precipitates; (3) the solubility of the controlling solid phase; (4) the extent to which the ions can be complexed in solution; and (5) the oxidation or reduction of the metal species (Eichenberger and Chen 1982).

Hydrolysis data are important in assessing the risks from organic chemicals having hydrolyzable functional groups (i.e. carboxylic acid, phosphoric acid and sulphonic acid, esters, amides, alkyl halides, carbamates, epoxides and phosphoric esters), in calculating estimates of kinetic rates for various compounds (including structure-activity relationships data) and in predicting the half-lives of organic chemicals in aquatic systems (Connell and Miller 1984).

IV.4.4 Ion Exchange

The process of ion exchange involves the exchange of ions adsorbed on a surface with ions in water. In practice, the distinction between adsorption and ion exchange is blurred because adsorption and desorption frequently result from the ion-exchange process (Matthess and Harvey 1982). Ion exchange affects the mobility and fate of chemical substances in water. It exerts an important control on water chemistry at the water-sediment interface (Drever 1982).

The nature, degree and rate of ion exchange depend on the properties of the dissolved ions and those of the available complementary ions. In general, the higher the ion's valence, the greater its affinity for sorption. Bonding strength is governed by the variations in pH. The process of ion exchange is also regulated by time, as it depends on the type of bond that develops, as well as temperature, the presence and concentration of competing ions and the selective properties of individual sorbents (Matthess and Harvey 1982). The relative ease of exchangeability is given by the series $Li^+ > Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, where lithium is held with the least force and barium the most (FAO 1979).

Clay minerals, iron hydroxides, manganese oxides and organic matter can sorb cations in water and release an equivalent amount of cations back into solution (Horowitz 1985). These processes are important in altering the composition of natural waters (Stumm and Morgan 1970). Oxides and organic matter, which frequently coat clay minerals, often have high exchange capacities (Drever 1982). Heavy metals can be released from clays depending on the prevailing conditions of the solution. The ion-exchange capacity (amount of exchangeable ions) of the silt can be exceeded such that metals in water may remain in the free and soluble (and biologically available) form (Golterman 1975; Matthess and Harvey 1982). Ion exchange also affects the fate of organic compounds in water. The pesticides paraquat and diquat, for example, may be removed from water by cation exchange with organic matter and clay minerals (Connell and Miller 1984).

IV.4.5 Microbial Degradation

The biodegradation of pollutants by microorganisms (e.g. bacteria, fungi, protozoa and algae) is an important removal and transformation process in water and in sediments. Information concerning biodegradation processes is critical to evaluating persistence, particularly for organic compounds likely to be solubilized or dispersed in or on water. The reactions associated with these processes include oxidation, reduction, hydrolysis and, occasionally, rearrangements. These reactions are a function of the molecular structure and concentration of the substance, size, type and growth rate of microbial assemblages, nutrients available, environmental characteristics (pH, ionic strength, oxidation-reduction conditions, etc.) and temperature. They are complicated by the nature, dynamics, viability and metabolic status of the microorganism populations (Connell and Miller 1984; Burns and Baughman 1985; Neely and Blau 1985a, b).

In most large bodies of water, the water column is stratified into several layers, each of which differs in temperature, availability of light, nutrient content and oxygen concentration. In general, the upper portion of the column is considered aerobic and the deeper region anaerobic. The sediment may also be stratified into oxidized and reduced layers. Each layer may be expected to contain different types of microbial populations with distinct metabolic activities (Neely and Blau 1985b). Bottom sediments tend to be a significant reservoir of organic and inorganic nutrients because of deposition of decaying organic matter. Bacterial population density within the sediment may be several orders of magnitude higher than that found in the water column (Neely and Blau 1985a).

Specialized microbial populations play an important role in the degradation of organic molecules in aquatic environments. Because no single microbial species possesses all the required enzymes to degrade the variety of both naturally occurring and synthetic organic compounds, biodegradation involves the actions of many diverse microbial populations, with separate but complementary capabilities (Neely and Blau 1985a).

On exposure to an organic substance, the microbial population may respond by:

1. immediate use of the substance as a carbon or energy source as the enzymes required for transport and metabolism of the substance are available or readily inducible;
2. lag or adaptation period prior to degradation because of: (i) induction or derepression of specific enzymes present at low or nonexistent levels in the population before exposure; (ii) genetic selection for new metabolic capabilities; and (iii) increase in numbers of organisms capable of a specific transformation;
3. degradation by processes of cooxidation or cometabolism (degradation of substances despite nonuse as growth substrates); and
4. slow or nondegradation because of such factors as physical inaccessibility or unfavourable environmental conditions (Neely and Blau 1985a).

The action of microorganisms on natural and synthetic compounds may bring about one or more of the following processes: mineralization, detoxification, cometabolism and activation. Mineralization involves the conversion of an organic compound into inorganic products. Detoxification refers to the conversion of a toxic substance into innocuous metabolites. Cometabolism involves microbial metabolism of a compound that the microorganism(s) cannot use as a nutrient. Activation is the conversion of a nontoxic compound into one that is toxic (Alexander 1980).

Partial degradation may result in a less toxic compound; a compound more toxic than the parent compound; a toxic compound, whereas the original molecule was nontoxic at environmental concentrations; a more persistent compound than the parent compound; or a compound subject to biomagnification or to changes different from those of the parent compound (Alexander 1980).

Microbial activity may also enhance the release of metals from sediments by formation of compounds capable of complexing metal ions. A major concern of microbial activity relates to the conversion of inorganic metal compounds to organometallic molecules as a result of enzyme-catalyzed oxidative and reductive processes. The formation of methyl compounds of, for example, arsenic, lead, mercury, selenium and tin provides one means of the release of highly toxic substances to the environment (Golterman *et al.* 1983).

Microbial degradation may be expressed by two equations which are based on Monod kinetics. If the concentration of toxic substance [C] is high (where [C] is much greater than the concentration of substrate supporting half-maximum specific growth rate (0.5 μmax)), then the biodegradation rate is a function of the microbial population only, and the equation is:

$$\frac{d[C]}{dt} = -K'_b[X]$$

where K'_b = biomass degradation rate constant
[X] = biomass concentration.

When [C] is very low, the relation is expressed as:

$$\frac{d[C]}{dt} = -K_{b2}[C][X]$$

where K_{b2} = a second-order rate constant (Neely and Blau 1985b).

There are limitations associated with the application of Monod kinetics to mixed culture and environmental systems. Typically, an acclimation period occurs between the time of exposure of unacclimated microorganisms to the chemical and the initiation of microbial action (i.e. until the enzymes necessary to effect some transformation are expressed or biodegradation organisms are developed by mutation). Monod kinetics are more applicable to acclimated organisms (U.S. EPA 1979; Alexander 1980; Connell and Miller 1984).

Not all synthetic organic molecules will be amenable to microbial degradation. If the microbial enzymes necessary for metabolism are absent or the substance protected in some way by the physical and chemical properties of the environment, the compound will persist. Persistence may range from several months to years (Alexander 1980).

IV.4.6 Oxidation-Reduction

Oxidation and reduction processes are often referred to as processes losing and gaining electrons, respectively. If water has an oxidative or reducing capacity, it can be described by the redox potential, that is, a numerical index of the intensity of oxidizing or reducing conditions within a system. Positive potentials indicate a relatively oxidizing state, and negative potentials indicate relatively reducing conditions (Hem 1985).

The chemical forms of many pollutants are modified by their oxidation-reduction properties and by the oxidizing and reducing characteristics of the environment in which they are found (Connell and Miller 1984). For example, the biogeochemical cycling of iron and, to a lesser degree, manganese is influenced by the spatial and temporal variations of the redox conditions of the water body (Wetzel 1975).

Photosynthesis and bacterial degradation of organic matter largely determine redox conditions in rivers and lakes. In photosynthesis, carbon dioxide is converted to organic matter and oxygen. The organic matter is composed of high free energy and nonequilibrium concentrations of C, N and S compounds (Drever 1982).

The composition of the organic matter in plankton may be represented by C_{106}, H_{263}, O_{110}, N_{16}, P_1 (Redfield *et al.* 1963). Photosynthesis may be expressed by the equation:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ + \text{(trace elements, energy)} = C_{106}H_{263}O_{110}N_{16}P_1 \text{ (algae)} + 138O_2$$

If molecular oxygen is available the products of bacterial respiration and decomposition are essentially the reverse of those of photosynthesis. During respiration, carbon is released as CO_2. This causes an increase in P_{CO_2} and a corresponding decrease in pH.

In the absence of molecular oxygen, decomposition of organic matter proceeds by a series of reactions which yield successively less energy. Some of the more important reactions follow:

1. Denitrification: through a series of reactions, bacteria oxidize organic carbon to CO_2 using the oxygen from the nitrate ion.
2. Deamination of amino acids: under aerobic conditions, amino acids will decompose as follows:

   $$\text{[amino acids]} = \text{[N-free compounds]} + NH_3$$

   The NH_3 forms NH_4^+ (i.e. $NH_3 + H_2O + CO_2 = NH_4^+ + HCO_3^-$) and causes a net increase in pH.
3. Sulphate reduction: bacteria oxidize organic matter to CO_2 using the oxygen from SO_4^{2-}, as expressed by:

   $$SO_4^{2-} + 2C_{organic} + 2H_2O = H_2S + 2HCO_3^-$$

   The by-product H_2S is toxic to most biota. The reduction of ferric oxides may occur and results in the release of phosphates and heavy metals adsorbed to the oxides.
4. Fermentation reactions: bacterial fermentation can occur at various $p\epsilon$ values (measure of redox intensity), and depends on the particular organic compound.

All anaerobic decomposition reactions are mediated by specialized bacteria. Their function is to catalyze the conversion of thermodynamically unstable compounds to more stable ones (Drever 1982). Each type of reaction occurs sequentially, with the reactions resulting in the most energy to the bacteria occurring first.

There may be substantial differences in redox environment throughout a specific body of water. In lakes, redox conditions result from the balance between the decomposition of organic matter and the concentration of dissolved oxygen. During overturn, the concentration of dissolved oxygen is regulated by equilibrium with the oxygen in the atmosphere. When the lake becomes stratified, the hypolimnetic concentration of dissolved oxygen decreases because of the decomposition of organic matter settling from the epilimnion. The total amount of organic matter falling into the hypolimnion during stratification will determine whether these waters will become anaerobic. In an oligotrophic lake, the supply of nutrients is low and so is photosynthetic production; the water is oxygenated at all depths and the $p\epsilon$ remains high. In eutrophic lakes, where productivity is high, the hypolimnion may become anaerobic. Under these conditions, the $p\epsilon$ will decrease with depth and with time from stratification (Drever 1982). The sequence of redox reactions under these conditions may include aerobic respiration; denitrification; nitrate reduction; reduction of manganese oxides; fermentation reactions; sulphate reduction; and methane formation (Westall and Stumm 1980). During overturn of this type of eutrophic lake, hydrogen sulphide and other compounds, such as heavy metals, may be mixed into the epilimnion.

At the water-sediment interface, where oxygen may be brought by turbulent transport, an oxidized microzone several millimetres in depth will develop. Microzone conditions are determined by diffusion of oxygen from the water and the biochemical reduction occurring in the sediment. The oxidized microzone influences the quantity and nature of the substances leaving the sediment and diffusing into the overlying water. Depending on the type and depth of the water body, the oxidized microzone tends to thin and may finally disappear as the supply of oxygen is decreased, whether by stratification or by oxidation of substances. At low redox, the presence of compounds such as Mn^{2+}, Fe^{2+} and H_2S changes local conditions (Wetzel 1975; Golterman 1975). For example, the solubility of metals that normally precipitate as hydroxides may increase, and phosphorus may be released from sediments because of dissolution of ferric hydroxide and oxides onto which the phosphorus is adsorbed (Connell and Miller 1984).

IV.4.7 Photolysis and Phototransformation

Photochemical transformations induced by sunlight may occur by one or more processes, depending on the structure of the chemical and the presence of other substances (U.S. EPA 1979). For these changes to occur, however, sufficient radiation energy must be absorbed to overcome the bond energies and allow dissociation.

Photochemical changes occur by two principal mechanisms:

1. direct absorption (direct photolysis) of light by the substance followed by reaction; or
2. electron or energy transfer (indirect photolysis) through an intermediate (photosensitizer) (Moore and Ramamoorthy 1984).

The direct absorption of sunlight can result in cleavage of bonds, dimerization, oxidation, hydrolysis or rearrangement (Zepp 1980). In an effort to predict photolysis rates as a function of the time of day, season, location and water depth, equations have been developed using solar irradiance, quantum yield and the absorption spectra of pollutants (Zepp and Baughman 1978). If pollutant concentrations are low, the rate of direct photolysis of chemicals (K_p) in water can be represented by a simple first-order expression (i.e. the rate is directly proportional to pollutant concentration):

$$K_p = K_a \Phi$$

where Φ = the reaction quantum yield

K_a = a rate constant for absorption of light by the chemical (which is a function of the photon flux, the distribution of light and the light absorption coefficient of the chemical) (Connell and Miller 1984; Zepp 1980); the first-order rate constant depends on light intensity which varies with time of day, season and latitude (U.S. EPA 1979).

The rate of photochemical oxidation by indirect photolysis may be expressed by (Connell and Miller 1984):

$$-\frac{dA}{dt} = K_{ox}[Ox][A]$$

where K_{ox} = second-order rate constant for reaction to the oxidant with compound A
[A] = concentration of the pollutant
[Ox] = concentration of the oxidant.

The rates of direct and indirect photolysis are influenced by the colour and clarity of the water body. Indirect photolysis will be affected by colour, clarity and concentrations of natural sensitizers and singlet oxygen (NRCC 1981).

Suspended sediment influences photolysis in water by: contributing to light attenuation; scattering light, which in turn diffuses downwelling radiation; affecting partitioning processes; and removing pollutants from underwater light by sorption to sediment settling downward. Vertical mixing in lakes also affects the amount of light received by a pollutant. Pollutants in the epilimnion will remain in that layer until the overturn, when they are mixed more deeply into the water body. Below the thermocline, photolysis occurs slowly, if at all, and, as long as the water body is stratified, upward mixing to the photic zone is slow (Zepp 1980).

The assessment of indirect photolysis is complicated by the fact that many photochemical processes may be involved and that the molecular structures of the photosensitizers that mediate indirect photolysis have not been identified. In a photosensitized reaction, light absorbed by a sensitizer molecule (e.g. humic matter) in water results in an excited state that can transfer its energy efficiently to another compound in water via a series of complex and competitive processes given certain conditions. The exact nature of the pathways of this process remains to be determined (Zepp 1980). The photochemical decomposition of pesticides, for example, may proceed by means of a series of photolytic reactions, including photooxidation, photonucleophilic hydrolysis and reductive dechlorination. These reactions will be influenced by factors such as the presence of natural photosynthesizers, pH and dissolved oxygen (Connell and Miller 1984).

Other transformations by indirect photolysis involve reactions with chemical oxidants, such as peroxy and hydroxyl radicals and singlet oxygen. Singlet oxygen, for example, may react with olefins, dienes and polycyclic aromatic hydrocarbons (U.S. EPA 1979; NRCC 1981).

In theory, the sum of the rates of direct and indirect photolysis results in the net rate of photochemical transformation. The net rate can be limited by the transport of the pollutant into the sunlight zone. When both direct and indirect photoreactions may be expressed as first-order reactions, the photolytic half-life ($t_{\frac{1}{2}}$) of chemicals can be expressed by (Zepp 1980):

$$t_{\frac{1}{2}} = \frac{0.69}{(K_d + K_s)}$$

where K_d = rate constant for direct photolysis
K_s = rate constant for indirect photolysis.

IV.4.8 Precipitation and Coprecipitation

Under different physical and chemical conditions, minerals will dissolve in or react with water. The chemical properties of minerals will be changed by dissolution reactions, which release constituents into water, and precipitation reactions, which remove them from water. The extent to which a compound will precipitate can be determined from the solubility-product constant. Both the rate and extent of precipitate formation will depend on the compound and the prevailing local environmental conditions (Lee and Jones 1983).

Precipitation reactions in natural waters largely involve carbonate and hydroxide salts; other salts, such as sulphates, phosphates, chlorides and silicates, may also be precipitated. Ferric iron and Mn(IV) often precipitate as hydrous oxides. Many transitional metals form hydroxy complexes near pH 7 (Pagenkopf 1978). At higher pH, carbonate adsorption and coprecipitation are important removal processes for Zn, Co, Cd and Pb (Pagenkopf 1978; Connell and Miller 1984).

Coprecipitation is the simultaneous precipitation of an otherwise soluble component and an insoluble salt (Pagenkopf 1978). Coprecipitation occurs as isomorphic inclusion, surface adsorption, solid-solution formation and occlusion. Isomorphic inclusion occurs when an ion of similar dimensions and chemical properties fits into the structure of the precipitate without causing significant disruption of the crystal structure of the precipitate. Hydrous oxides and other solids have a large surface area and can adsorb large quantities of other ions. In solid-solution formation, the solute dissolves within the solid solution. With occlusion, solutes are trapped within the crystal lattice of the precipitate. Coprecipitation and replacement processes are important in removing trace metals from water in a more stable phase (e.g. copper coprecipitation with ferric hydroxides) (Matthess and Harvey 1982).

IV.4.9 Solubility

The solubility of a substance represents the total amount of solute species that will remain permanently in solution under a given set of conditions (i.e. temperature and pressure). It is an intrinsic property of a substance and helps to determine its distribution in solution (Verschueren 1983; Connell and Miller 1984).

The solubility product (Ks) refers to the product of the concentrations of the ionic species involved in a dissolution. It may be calculated when equilibrium is established between the solid and solute phase of a substance under specific conditions. The Ks is a constant and may be used to estimate the comparative ability of a compound to go into solution. Under natural conditions, equilibrium is rarely reached. Equilibrium solubility can be shifted by variations in competitive ions and organic substances in solution (Waite 1984).

The solubility of individual substances helps to determine the activity of dissolved substances and the degree of complex formation (Pagenkopf 1978). Environmental factors, such as pH, redox conditions, temperature, hardness and the presence and nature of dissolved solids and organic matter, affect the solubility of a substance in water (Stumm and Morgan 1970; Mullins 1977). A chemical's water solubility will, in turn, affect its susceptibility to hydrolysis, photolysis, complexation, volatilization, oxidation, reduction and biodegradation (Verschueren 1983).

For gases, the solubility of both electrolyte- and non-electrolyte-forming gases in solution is commonly described by Henry's constant. The more soluble gases, such as SO_2, may form electrolyte solutions. The solubility of non-electrolyte-forming gases, such as oxygen, may be inversely proportional to the vapour pressure at the system temperature. The solubility is also strongly dependent on temperature, usually decreasing as the temperature rises (Mackay 1980).

In some systems, the concentrations of many metal ions are controlled by the solubility of metal carbonates and hydroxide complexes (Stumm and Morgan 1970; Pagenkopf 1978; Connell and Miller 1984). The soluble forms of metals are usually ions, simple or complex, or un-ionized organometallic chelates or complexes.

In general, for most inorganic salts, an increase in temperature will result in an increase in solubility. Some exceptions, such as calcium sulphate and sodium sulphate, show the opposite relationship.

The solubility of many organic substances may be determined by (1) the nature of the interactions in solution between the substance and water (i.e. hydrophobicity); and (2) in the case of a solid, its melting point relative to the system temperature. Many organic solutes tend to form colloidal particles in water, which may result in concentrations of several milligrams per litre, thereby masking the true dissolved concentration (Mackay 1980). Studies also suggest a strong inverse correlation between water solubilities of organic compounds and the octanol-water partition coefficient (Verschueren 1983).

IV.4.10 Sorption

Adsorption is a process where a dissolved ion or molecule is concentrated on the surface of a preexisting solid substrate. It is often the reason for finding lower concentrations of trace metals in natural waters than would be expected by equilibrium solubility calculations (Pagenkopf 1978; Drever 1982). The tendency for a substance to sorb onto particulate surfaces is an important factor affecting its mobility and ultimate fate in waters (Verschueren 1983).

The materials available as sorbents include clay minerals, inorganic and organic colloids (gels of ferric hydroxide, manganese hydroxide and silicic acid; humic colloids) and the surfaces and integuments of living and dead organisms (Ruttner 1953; Mill 1980). The extent of sorption of a compound from water onto a solid is a function of (Pagenkopf 1978; Verschueren 1983):

1. factors regulating equilibrium (e.g. temperature, atmospheric pressure and ionic strength);
2. physical and chemical characteristics of the sorbent;
3. the surface area of the solid; and
4. the nature and distribution of the binding sites on the surface.

There are different types of sorption, ranging from adsorption by Van der Waals forces, which exert only a weak bond between the solute and the sorbent, to chemisorption, which involves more definite chemical interaction (Pagenkopf 1978).

Sorption processes play an important role in the control of metal and organic compound concentrations in water. The adsorption of metal ions is strongly pH-dependent, and enhancement occurs when the metal ion hydrolyzes. For example, hydrous oxides of iron and manganese affect concentrations of Mn, Fe, Co, Ni, Cu and Zn in water; diquat and paraquat adsorb to clay, and cadmium to humic matter (Pagenkopf 1978; Connell and Miller 1984).

The tendency for sorption of a dissolved organic onto surfaces is related to its hydrophobicity. In general, the lower the solubility of the substance, the greater its tendency for adsorption (Pagenkopf 1978; Mill 1980). The characteristics influencing pesticide adsorption to soil colloids depend on the characteristics of the pesticide, such as the type of functional groups associated with the organic molecule, configuration of the molecule, water solubility, ionization, polarity and charge distribution on cations (Pagenkopf 1978; Connell and Miller 1984).

A dynamic equilibrium is established between the substance in water and that adsorbed on the surface. One of the more common expressions of the graphic representation (adsorption isotherm) of the equilibrium is that developed by Freundlich (U.S. EPA 1979):

$$C_s = K_p C_w^{1/n}$$

where C_s = concentration of compound in particulate phase
C_w = concentration of compound in water phase
K_p = partition coefficient for sorption
$1/n$ = exponential factor.

The measurement of K_p must account for equilibrium between phases, because uptake is usually rapid and involves weak bonds, whereas the next phase results in relatively strong binding and slow desorption.

The equilibrium ratio of sorbed to nonsorbed compound on a sediment can be expressed as an equilibrium constant (Mill 1980):

$$K_s = [C]_s/[C]_w \text{ (at constant temperature)}$$

The values of K_s for an individual compound may vary depending on the composition of the sediment. To place all sediments on a more comparable basis, the K_s may be expressed as:

$$K_s = AK_{sc}$$

where A = fraction of organic content (mg C per mg sediment)
K_{sc} = sorption constant adjusted for organic content.

If A = 1, then the octanol-water partition coefficient (P_{ow}) can replace K_s (Mill 1980). This is important, because studies show a close direct relationship between K_{sc}, solubility, bioconcentration and the organic carbon content of sediments (U.S. EPA 1979; Mill 1980).

Whereas processes based on chemical combinations largely depend on stoichiometric ratios and nonreversibility of the product, adsorption is a function of equilibrium and, therefore, is theoretically reversible. With decreases in the concentration of the substance in water, the amount adsorbed also decreases. Compounds sorbed from waters can theoretically return to water and hence become available to organisms (Ruttner 1953). Alternatively, if the portion of compound sorbed to sediments or soil is large, other transformation processes affecting the overall rate of loss of the compound will be modified, for sorption serves to buffer the concentration of compounds in water (Mill 1980).

IV.4.11 Volatilization

Volatilization refers to the change of state from a solid or liquid phase to the vapour phase, and subsequent movement by advection or diffusion (Neely and Blau 1985b). It is recognized as an important transport process for many chemicals characterized by low solubility and low polarity (Mackay *et al.* 1980).

Transport of a compound from sediments or the bottom of lakes or rivers to the atmosphere depends on a series of stages and controlling rates (or resistance). These stages of diffusion may include (1) release from sediments; (2) diffusion through the layers of the lake hypolimnion, thermocline or epilimnion; (3) diffusion to interface through the liquid surface film; (4) transfer across the interface; and (5) diffusion through the atmospheric film to the atmosphere. Diffusion from the bottom of a river is usually considered to occur quickly because of the effect of river current. For shallow lakes, stages (3) and (4) are the likely rate-controlling processes for transfer of chemicals, because they are slower than vertical diffusion through the epilimnion (Mackay *et al.* 1980). The rates of volatilization are also influenced by water turbulence and wind speed (NRCC 1981).

The relative volatility of organic chemicals from water can be derived based on vapour pressure and water solubility (Hamaker 1972). In order to estimate the absolute vaporization rate of low-solubility organics from water, Mackay and Leinonen (1975) elaborated on Hamaker's concept. Their work indicates that the water-air partition ratio of the organic chemical (calculated from its vapour pressure and solubility) will determine whether the liquid- or vapour-phase resistance controls the rate of vapour loss. The calculations show that most organic substances of low solubility will rapidly vaporize from water in the absence of clay or organic colloids (Spencer and Farmer 1980).

Experiments show that sorption-desorption processes and the rate at which they occur may control whether or not a sorbed solute is volatilized from water which is brought to the surface for a short time. Dissolved solutes will volatilize during exposure if the half-life of volatilization exposure at the surface is less than desorption time. If desorption is fast, volatilization of the sorbed material will occur after it is desorbed. In general, the dissolved solute will volatilize at the surface, whereas that sorbed will desorb later in the bulk of the water column and establish a new equilibrium.

Sedimenting sorbents will usually enhance downward diffusion at a rate that is a function of sorbed concentration and settling velocity. If the sedimentation velocity through the water column is low, the sorbent will likely maintain equilibrium concentrations of sorbate. Alternatively, if the velocity is high, equilibrium may not be reached. The impact of sorption on transport rates is complex, because by increasing concentrations, it decreases resistances and increases diffusion rates (Mackay *et al.* 1980).

The principal variables for calculating the volatilization rates of solutes from lakes and other water bodies are those describing the phase equilibrium (i.e. Henry's law constant or fugacity capacities, refer to articles by Mackay and Paterson 1982, 1984), those describing the kinetics of the system (in terms of resistance, mass transfer coefficients and diffusivities) and those describing the physical and chemical properties of the solute (i.e. sorption and air/water partition properties) (Mackay *et al.* 1980; Mackay 1981).

IV.5 FACTORS THAT MODIFY TOXICITY TO AQUATIC ORGANISMS

Various characteristics of water and of organisms may change the toxicity of water pollutants to aquatic organisms. Both abiotic and biotic characteristics act as modifying factors. Abiotic factors include the physical and chemical characteristics of the water. The biotic factors consist of the features that relate to the organism, such as species, life stage, size, nutritional status, general health and degree of acclimation to natural environmental conditions or to the pollutant (Sprague 1985). A complete review of the information available on modifying factors is not attempted in this section. However, some of the major factors are covered, and the reader is encouraged to consult the literature for more detailed information.

IV.5.1 Effects of Abiotic Factors on Aquatic Life

IV.5.1.1 Temperature

Temperature acts on organisms in different ways. Aquatic organisms are adapted to the seasonal changes in the temperature of their particular habitat. Organisms may be capable of withstanding changes outside this range, especially those of short duration, although they may be adversely affected by rapid unnatural fluctuations within this range which do not allow time for acclimation (Warren 1971; Alabaster and Lloyd 1984).

Particularly in poikilotherms, temperature changes affect movement, metabolic and respiratory rates, behaviour and all stages of reproduction, such as gonad development and growth rates (Warren 1971; Alabaster and Lloyd 1984). Some species, for example, may rely on climatic events to stimulate physiological cues for production of offspring at the most favourable times. Furthermore, the speed of development, activity or reproduction may be important in the presence of competitors and predators as well as to species that have several generations in one season (Macan 1974).

Different species have different temperature optima for growth, and, depending on the degree and duration of temperature change, certain species may be favoured. Many species do not occupy the whole range which their temperature tolerance would permit because, towards the extremities, they encounter species with a similar way of life, but a different temperature optimum. The second species may move faster, eat faster, utilize food more efficiently or breed faster and basically outcompete the first species (Macan 1974). This can lead to a change in the composition of the aquatic community. Tolerance limits can change over the lifetime of the aquatic organism, and it can become acclimated to a different temperature regime. This capability, however, could be affected by the presence of pollutants (Warren 1971) (see also IV.3.8).

IV.5.1.2 Dissolved Oxygen

The sensitivity of aquatic organisms to low concentrations of dissolved oxygen differs among species, life stages (e.g. eggs, larvae, adults) and according to activity (e.g. feeding, growth, reproduction) (Alabaster and Lloyd 1984). There can be wide variations during 24 h in the magnitude of dissolved oxygen concentrations, because of diurnal algal activity, and these will differ according to season and flow (Alabaster and Lloyd 1984; Sprague 1985).

Dissolved oxygen is required for aerobic respiration, and, if it decreases to low concentrations, it may become a limiting factor for the maintenance of life. The lower lethal limit depends on the species. Depending on the intensity and duration of low dissolved oxygen concentrations, a change in species diversity may develop.

The ability to detect and avoid toxicants could be affected by low concentrations of dissolved oxygen (Alabaster and Lloyd 1984). Furthermore, the effects of toxicants may be magnified if the aquatic organism is under the stress of low or inadequate dissolved oxygen. Low concentrations of dissolved oxygen result in accelerated irrigation of respiratory surfaces, thus increasing the exposure of these surfaces to an increased amount of any toxicant present in water (Warren 1971; Sprague 1985). The increased ventilation rate may also cause gills to become clogged with suspended material; alternatively, gill surfaces could be damaged if the material is abrasive.

IV.5.1.3 Hydrogen Ion Concentration

The direct effects of pH on organisms become more severe as the pH tends away from the natural range (6.5-9.0). The reader is referred to Alabaster and Lloyd (1984) for a summary of these effects. In general, few fish can acclimate to pH 3.5-4.0. Some fish species, such as perch and pike, may acclimate to this pH range, but most could not reproduce. In alkaline waters, pH 9.0-9.5 approaches the tolerance level for many fish, but most invertebrates are unaffected. A pH ranging from 9.5 to 10.0 may be lethal to salmonids over a long period of time (Sprague 1985).

IV.5.1.4 Particulate Matter

Suspended particles may affect aquatic systems by decreasing light penetration and hence reducing primary productivity. Studies show that high concentrations of suspended solids may kill fish directly by clogging and abrading gills, augment susceptibility of fish to diseases, restrict food availability to fish and affect growth rates, normal movements and migrations of fish, and inhibit egg development (Alabaster and Lloyd 1984). In addition, the blanketing effect of settling out results in abrasion and mortalities to benthic plants and invertebrates.

Particulate matter may sediment and be deposited to bottom sediments at rates depending on water turbulence and particle density. Turbulence conditions in the bottom layer will determine whether or not particles will remain permanently in the sediment.

Particulate matter may act as sorption agents for chemicals in the water column. Organic chemicals, nutrients and heavy metals may be sorbed to the surface of these particles, and hence their biological effects may be modified (Kranck 1980). In addition, bacterial degradation of material rich in organic matter may contribute to deoxygenation of bottom waters.

IV.5.2 Exposure

Aquatic organisms are exposed to pollutants in the water, in sediment and in food. Physiological processes within the organisms will influence the quantity of toxicant and metabolites in body fluids, tissues and organs. For example, phytoplanktonic algae manifest a large potential for accumulation of pollutants because of their surface exchange area exposed to the environment (Davies 1978). Molluscs and other filter-feeding organisms show potential for significant accumulation because of the constancy and intensity of contact with the pollutants, both in the water and from food sources (Boudou *et al.* 1983).

Fish may be directly exposed to pollutants through the skin and the respiratory epithelium. The latter presents a great area for surface exchange between the blood and the environment. Indirect exposure of fish to pollutants takes place in the gut and intestines (Boudou *et al.* 1983). Once absorbed, substances are distributed by the circulatory systems and by movement across membranes to various organs and tissues of the body (Connell and Miller 1984). Excretion occurs principally in the urine or bile.

Accumulation of pollutants in target organs depends on factors such as the physical and chemical properties of the pollutant, the level of irrigation and the sites for interaction with the organ. Organic compounds, such as PCBs and organochlorine insecticides, may be deposited in body fats. Starvation and stress conditions can result in rapid mobilization of these compounds back into the bloodstream causing damage to the nervous system or kidneys. Detoxification mechanisms may involve temporary or more permanent storage at inactive sites within organisms. Metals, for example, may be stored by binding to proteins, polysaccharides and amino acids in soft tissues or body fluids. Bone and exoskeleton provide more permanent storage for elements such as Pb, Cd and Hg (Connell and Miller 1984).

IV.5.3 Effects

Organisms differ in their susceptibility to pollutants. The uptake, distribution and elimination of chemicals by organisms are regulated by many intrinsic and extrinsic factors. Intrinsic factors include rates and patterns of metabolism. Dietary factors will influence the toxicity of substances by producing changes in physiological and biochemical functions. In addition, the physical activity, ability to acclimate and physiological state (e.g. spawning, molting, in transit from salt water to fresh water) of organisms, age, sex, species and strains of organisms also affect susceptibility (Connell and Miller 1984; Rand and Petrocelli 1985). Extrinsic factors relating to the physical and chemical characteristics of the water have been discussed previously.

Adverse effects may result from short- or long-term exposure to toxic substances. The specific response of an organism to a pollutant may be assessed in terms of the magnitude of the effect (including whether or not it occurs) and the time required for its expression (e.g. acute and chronic effects relative to the organism's life span) (Connell and Miller 1984). Lethal or sublethal effects may result from a single challenge or from repeated or long-term exposures. The latency period for the detection of these effects may be quite long, particularly if exposure is to low concentrations (Rand and Petrocelli 1985).

Sublethal effects may indirectly lead to reduced chances of survival or reproduction in natural populations, as well as causing shifts in species composition and diversity (Connell and Miller 1984). Sublethal effects may be behavioural, for example, alterations in learning ability or responses to natural stimuli; physiological, for example, effects on growth and impaired reproductive success; or biochemical, for example, modified brain cholinesterase and electrolyte concentrations (Connell and Miller 1984; Nicholson 1984). They may be reversible, and diminish or cease with time; reversible interactions, between the substance and the biological substrate or receptor, usually leave the substance and receptor unaltered. Irreversible effects include carcinogenic and mutagenic reactions involving alterations of DNA molecules. Over a long period of time, sublethal effects may introduce subtle changes in behaviour, biochemistry, morphology, resistance and reproduction which will affect an organism's ability to survive (Connell and Miller 1984; Rand and Petrocelli 1985).

In general, adverse effects may occur immediately or may be delayed, depending on the intrinsic characteristics of the organism and on the properties of the substance and possibilities for biotransformation within the organism. They may be local or systemic, sequential or simultaneous, as well as subject to toxicological interaction (e.g. additivity, antagonism, synergism) (Rand and Petrocelli 1985).

An organism's response to individual pollutants may differ from that to multiple pollutants. Multiple toxicity, for example, covers a full range of effects, from antagonism to synergism. A strictly additive interaction between two substances occurs when the mixture proves to be just as toxic as the sum of the two solutions tested separately. Variations on this type of interaction will depend on the degree of additive action (e.g. infra- or supraadditive). Antagonism, in which the toxicity of the mixture is less than would be expected were there no interaction between the two substances, may be competitive (one toxicant displaces another from its site of action); chemical (one substance inactivates another through chemical interaction, as in the chelation of some metals); functional (two substances act on the same cell system, but contribute in differing ways to a particular response in the cell); and physiological (substances act on different cell systems and produce opposing effects) (Warren 1971; Connell and Miller 1984). Synergistic interactions refer to the enhanced toxicity of one substance in the presence of another substance. The mechanisms of synergistic toxicity are not fully understood but some theories have been advanced (e.g. increased rate of uptake; reduced excretion rates; changes to detoxification mechanisms) (Alabaster and Lloyd 1984; Rand and Petrocelli 1985). The effects of mixtures of a number of specific pollutants are discussed in Alabaster and Lloyd (1984).

To date, adequate information from which to establish a general approach for evaluating and predicting joint toxicity is lacking. The study of the effects of mixtures on fish and other organisms often involves using predictive models (Mackay 1982).

IV.5.4 Mechanisms of Toxicity

Substances may interact with the cell at any of the steps maintaining normal cell functions. The actions of toxic substances may increase or decrease the passage of substances into the cell for energy production or maintenance of the osmotic and electrical balance of the cell; the substances may also react with enzymes or the metabolites of enzymatic reactions (Warren 1971; Connell and Miller 1984).

For example, the toxic mechanisms for metal ions generally fall into three categories (Connell and Miller 1984):

1. blocking of the essential biological functional groups of biomolecules (e.g. proteins and enzymes);
2. displacement of essential metal ions in biomolecules; and
3. modification of the active conformation of biomolecules.

Some studies suggest that chlorinated hydrocarbons act by dissolving the fatty membrane surrounding nerve fibres and interfering with the transport of ions in and out of the fibre. For organophosphates, the site of toxic action is the synaptic gap of nerves. Organophosphates and carbamate pesticides deactivate the enzyme acetylcholinesterase (AChE) which normally breaks down acetylcholine once it has carried the impulse across the synaptic gap. Inteference with the breakdown process results in an accumulation of acetylcholine and a series of extraneous nerve impulses (tremors, convulsions, paralysis) (Mullins 1977). Other pesticides (e.g. organochlorine insecticides) often induce increased activity of hepatic enzyme systems at extremely low levels of exposure. This activity may influence other metabolic processes and cause synergistic or antagonistic effects through stimulation of enzyme systems responsible for metabolizing pesticides.

IV.5.5 Importance of Membranes

Membranes control the movement of dissolved substances through concentration gradients on either side of the membrane boundaries. The distribution of a contaminant is therefore highly dependent on its ability to cross biological membranes. Transport mechanisms include passive diffusion, filtration, active transport, facilitated diffusion and pinocytosis (Connell and Miller 1984).

Passive diffusion can occur across a membrane that is permeable to the chemical and across which a concentration gradient exists. Special transport includes both active and facilitated transport. Both processes regulate essential metals, sugars and amino acids. The following characterize the active transport system: (1) chemicals move against electrochemical gradients; (2) at high substrate concentrations the transport system is saturated and a transport maximum is exhibited; (3) the transport system is selective; and (4) the system requires an expenditure of energy (Connell and Miller 1984; Spacie and Hamelink 1985). Facilitated diffusion involves carrier transport, except that the substrate does not move against a concentration gradient, and the process requires no cellular energy input.

Biological membranes consist primarily of lipids. The predominant factors influencing the movement of substances across these membranes are lipid and water solubility, polarity, chemical stability, molecular weight of the substance and degree of ionization. The rate of movement of the substance through the organism will be influenced by the metabolic activity of the organism and extrinsic factors, such as water temperature, the presence of other parameters, pH and hardness (Hunn and Allen 1974).

Lipid solubility is frequently characterized by the octanol-water partition coefficient (P_{ow}). The degree of accumulation and toxicity increase with increasing P_{ow}. The water solubility of organic substances has been correlated with accumulation in fish; as solubility decreases, accumulation increases (Zitko 1980).

In general terms, nonionized organic compounds penetrate biological membranes more easily than do ionized organic compounds. Weakly ionized inorganic compounds, such as hydrogen sulphide and ammonia, are very toxic to fish as undissociated molecules (Zitko 1980).

The P_{ow} is commonly used in the concept of structure-activity relationships because correlations have been observed between P_{ow} and the toxic characteristics of some chemicals (Haque *et al.* 1980). The qualitative structure-activity relationship concept is based on the changes in certain properties and biological activity of compounds as a function of substituents (Haque *et al.* 1980; Koch 1984).

IV.5.6 Bioaccumulation

The processes of uptake and retention of substances by an organism may result in high concentrations causing adverse effects in the organism. Information on the exposure concentration and on the processes of metabolism and release of a substance from the organism plays a key role in evaluating chemical hazard and risk (Haque *et al.* 1980).

Bioaccumulation may be considered as a balance between uptake and elimination. If the uptake is excessive, the homeostatic processes that control body levels of substances and tissue distribution may be inhibited, and bioaccumulation may occur, because uptake exceeds the rate of depuration (Connell and Miller 1984).

Substances must be in a dissolved form for transport into biological membranes. The bioavailability of dissolved substances is decreased by sorption to suspended solids, sediments, humic acids and other macromolecules, formation of colloidal suspensions, chelation, complexation and ionization.

The process of bioaccumulation is used to explain the transfer of substances through the trophic levels of the aquatic food web. A toxicant, for example, although present in only trace quantities in the water, can exert a large biological effect if it is selectively taken up and accumulated in an organism's tissues (bioconcentration) (Dagani 1980). The concentration of a substance at each level may be estimated from the bioconcentration factor for the level plus the substance contributed by feeding on the next lower level. The bioconcentration factor is a measure of the tendency of a substance to concentrate in aquatic organisms (Neely *et al.* 1974). It can be related to the lipophilicity and water solubility of the compound and to physical and chemical equilibrium measurements, such as the *n*-octanol-water partition coefficient. Organic substances of low solubility in water, for example, may be stored and concentrated in the fatty tissues of organisms. In aquatic environments, the concentration of the substance may vary with time because of hydrolysis, evaporative loss and other degradation processes. These factors influence the tendency of the substance to reach equilibrium between water and the biophase. Slow diffusion to the lipid site and metabolic breakdown in the organism may also affect the establishment of an equilibrium between water and the biophase (Chiou 1981).

Octanol-water partition coefficients are used in the calculation of P_{ow} for compounds that are structurally similar by adding contributions for groups of various types in various locations. The structure-activity (SA) concept is based on the variation in certain properties and biological activity of chemicals as a function of substituents. A correlation has been observed between the P_{ow}, as a function of a homologous series, with certain toxic characteristics. The concept, however, is applicable to a series of chemicals where the basic skeleton of the molecule is identical, but variations are due to changes in the functional groups and substituents (Haque *et al.* 1980). The relationships among molecular structure, fate and toxicity of these compounds are used as a basis for predicting the fate and toxicity of nontested chemicals and for qualitatively interpreting their action (Haque *et al.* 1980; Koch 1984).

IV.5.7 Biomagnification

Biomagnification results from the retention and concentration of a substance that is resistant to degradation through the trophic levels of the food web. The extent of biomagnification is a function of the number of stages in the food web; the kinds of organisms in the food web; the substance being bioaccumulated; the dose of substance at each level of the web; and the time of contact with the substance (Ray and Trieff 1980).

IV.5.8 Biotransformations

Many organisms have metabolic pathways capable of deactivating and/or activating substances (e.g. biodegradation, detoxification and metabolism) (Connell and Miller 1984; Lech and Vodicnik 1985). These transformations may have dramatic effects on the physical, chemical, pharmacokinetic and toxicological properties of a substance. Numerous factors affecting physiological processes may influence biotransformations, e.g. diet, season, temperature, photoperiod, species, strain, life stage and sex. Although many of these factors have been studied, it is still difficult to accurately evaluate the contribution of these factors to biotransformations (Lech and Vodicnik 1985).

A variety of biotransformation reactions (e.g. oxidation, hydrolysis, reduction, conjugation) may occur in an organism, and the products that result from these reactions may behave differently from the parent component (Rand and Petrocelli 1985). The general mechanisms for many of these transformations are mediated by enzyme systems, and consist of formation of metabolites (usually mixed-function oxidations based on cytochrome P-450) and transformations into less toxic and more hydrophilic conjugates. Oxidation of foreign substances, for example, may occur by a cytochrome P-450-dependent mixed-function oxidase (MFO) system located in the endoplasmic reticulum of the cell; the NADPH-dependent oxygenases mediate the introduction of molecular oxygen into organic substrates (Zitko 1980; Connell and Miller 1984).

Other biotransformation processes include excretion of the substance and/or its metabolites without conjugation, by diffusion across cell membranes and occasionally by direct conjugation. For example, microorganisms excrete metabolites through the cell surface; plants conjugate pesticides and their metabolites with endogenous compounds and deposit them in vacuoles; animals excrete conjugates primarily in urine and bile (Connell and Miller 1984). Some transformations result in reactive metabolites, for example, the oxidation of aromatic hydrocarbons and olefins into intermediate arene or alkene oxides. Some of these metabolites may interact with the cell's genetic material and be involved as primary carcinogens and mutagens (Lech and Vodicnik 1985).

IV.5.9 Effects on Community Structure

Organisms in natural aquatic systems are continuously exposed to fluctuations occurring in their environment. Some species adapt to these changes, whereas other species are unable to. This causes changes in the productivity of the aquatic environment, as well as spatial and temporal changes in species composition and abundance. If, for example, sensitive species decrease, the structure of the community may be changed by a reduction in diversity. If the populations involved are substantial, the functioning of the community may be affected.

Many studies on aquatic toxicity relate to cause-and-effect relationships. These studies are an important tool in understanding and evaluating the potential hazard of chemicals. The predictability of toxic action, however, decreases from laboratory studies to the field situations involving population and community responses (Connell and Miller 1984).

Just as toxic effects on a population result from effects on individuals, the effects of toxic parameters on a community will result from differential effects on populations. Population density and species diversity may be altered by both direct and indirect exposure to a toxic substance. A sensitive population may be eliminated, either directly or by altering the individual's competitive ability and survival behaviour. A pollutant may adversely affect forage species of organisms, such as plankton and insects, which may be more susceptible to its lethal properties. Organisms that depend on these species as a food source are subsequently affected, and will be obliged to find a substitute or starve. Toxic substances may also indirectly alter the physical characteristics of the environment, thereby adversely affecting the survival of organisms (e.g. the use of copper sulphate (herbicide) may result in anaerobic conditions because of large quantities of decaying organic matter) (Meyers and Hendricks 1985).

Long-term sublethal effects on populations are difficult to document, for in natural populations the affected organisms are frequently eliminated through natural means (predation, secondary diseases, etc.). Effects such as disruption of sensory perceptions or interference in the functioning of the eyes by pollutants may produce chronic direct adverse effects on critical behaviour patterns such as migrations, escape and prey selection. Aberrant behaviour disrupts normal behaviour patterns, and, when associated with reproductive cycles, may endanger the survival of a population (Meyers and Hendricks 1985).

Under some conditions, where natural biological communities have been exposed to toxic substances for a relatively long period of time, it is possible for local populations to show genetic adaptation which allows certain species to persist under otherwise adverse conditions. This kind of adaptation has been studied under conditions of very long-term exposure to a consistent composition of heavy metals (Golterman *et al.* 1983). The ability to develop tolerance and adapt to polluted conditions is an advantage. However, tolerant organisms in highly contaminated areas may accumulate high concentrations of pollutants, and transmit these through the food web to other trophic levels with predatory species not so well adapted.

IV.6 REFERENCES

Alabaster, J.S. and R. Lloyd. 1984. Water Quality Criteria for Freshwater Fish. 2nd edition. Food and Agriculture Organization of the United Nations. 361 pp.

Alexander, M. 1980. Biodegradation of toxic chemicals in water and soil. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 179-190.

ASCE. 1972. Ground Water Management. Manuals and Reports on Engineering Practice. No. 40. The American Society of Civil Engineers, New York. 214 pp.

Babich, H. and G. Stotzky. 1983. Influence of chemical speciation on the toxicity of heavy metals to the microbiota. *In* Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, Inc., New York. pp. 1-46.

Birge, E.A. 1910. An unregarded factor in lake temperature. Trans. Wis. Acad. Sci. Arts Lett. 16: 989-1016. (Cited in Kwiatkowski 1984.)

Birge, E.A. and C. Juday. 1921. The inland waters of Wisconsin. The dissolved gases of the water and their biological significance. Wis. Geol. Nat. Hist. Surv. Bull. XXII. (Cited in Kwiatkowski 1984.)

Blair, A.H. 1974. Hydrogeological factors in ground water pollution. *In* Groundwater Pollution in Europe. J.A. Cole (ed.). Water Information Center, Inc. Port Washington, New York. 547 pp.

Borgmann, U. 1983. Metal speciation and toxicity of free metal ions to aquatic biota. *In* Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, New York. pp. 47-72.

Boudou, A., D. Georgescauld and J.P. Desmazès. 1983. Ecotoxicological role of the membrane barriers in transport and bioaccumulation of mercury compounds. *In* Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, Inc., New York. pp. 117-136.

Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press Inc., New York. p. 14.

Burns, L.A. and G.L. Baughman. 1985. Fate modelling. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 558-584.

Chiou, C.T. 1981. Partition coefficient and water solubility in environmental chemistry. *In* Hazard Assessment of Chemicals. Current Developments. Vol. I. J. Saxena and F. Fisher (eds.). Academic Press, Inc., New York. pp. 117-153.

Connell, D.W. and G.J. Miller. 1984. Chemistry and Ecotoxicology of Pollution. John Wiley & Sons, Inc., New York. 444 pp.

Dagani, R. 1980. Aquatic toxicology matures, gains importance. Chem. Eng. News 58: 18-23.

Davies, A.G. 1978. Pollution studies with marine plankton. Part II. Heavy metals. Adv. Mar. Biol. 15: 381-508. (Cited in Boudou *et al.* 1983.)

Demayo, A., A.R. Davis and M.A. Forbes. 1978. Forms of Metals in Water. Sci. Ser. No. 87. Inland Waters Directorate, Fisheries and Environment Canada, Ottawa. 24 pp.

Drever, J.I. 1982. The Geochemistry of Natural Waters. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 388 pp.

Duffus, J.H. 1980. Environmental Toxicology. Edward Arnold (Publishers) Ltd., London. pp. 105-107.

EIFAC. 1976. Report on Copper and Freshwater Fish. Prepared by European Inland Fisheries Advisory Commission Working Party on Water Quality Criteria for European Freshwater Fish with the Co-operation of the United Nations Environment Programme (UNEP), Food and Agriculture Organization, Rome. EIFAC Tech. Pap. No. 27.

Eichenberger, B.A. and K.Y. Chen. 1982. Origin and nature of selected inorganic constituents in natural waters. *In* Water Analysis. Vol. 1. Inorganic Species. Part I. R.A. Minear and L.H. Keith (eds.). Academic Press, Inc., New York. pp. 1-54.

Faust, S.D. and D.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. 400 pp.

FAO. 1979. Groundwater Pollution: Technology, Economics and Management. Publications Division. Food and Agriculture Organization of the United Nations, Rome. 137 pp.

Forstner, U. and G. Wittman. 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, New York. 486 pp. (Cited in Horowitz 1985.)

Freeze, R.A. and J.A. Cherry. 1979. Groundwater. Prentice-Hall Inc., Englewood Cliffs, New Jersey. 604 pp.

Frevert, T. 1985. Chemical limnology. *In* The Handbook of Environmental Chemistry. Vol. 1. Part D. The Natural Environment and the Biogeochemical Cycle. O. Hutzinger (ed.). Springer-Verlag, New York. pp. 83-124.

Golterman, H.L. 1975. Physiological Limnology. An Approach to the Physiology of Lake Ecosystems. Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. 489 pp.

Golterman, H.L., R.S. Clymo and M.A.N. Ohnstad. 1978. Methods for Physical and Chemical Analysis of Fresh Waters. Blackwell Scientific Publ., Oxford, Great Britain. 248 pp.

Golterman, H.L., P.G. Sly and R.L. Thomas. 1983. Study of the Relationship Between Water Quality and Sediment Transport. United Nations Educational, Scientific and Cultural Organization, Paris, France. 231 pp.

Hamaker, J.W. 1972. *In* Organic Chemicals in the Soil Environment. C.A.I. Goring and J.W. Hamaker (eds.). Marcel Dekker, New York. pp. 341-397. (Cited in Spencer and Farmer 1980.)

Haque, R., J. Falco, S. Cohen and C. Riordan. 1980. Role of transport and fate studies in the exposure, assessment and screening of toxic chemicals. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 47-67.

Hart, B.T. 1974. A compilation of Australian Water Quality Criteria. Australian Water Resources Council, Department of the Environment and Conservation, Canberra, Australia. Tech. Pap. No. 7. Res. Proj. No. 71/36. 187 pp.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. 3rd edition. Water Supply Paper 2254. U.S. Geological Survey, Alexandria, Virginia. 263 pp.

Horne, R.A. 1978. The Chemistry of Our Environment. John Wiley & Sons, Inc., New York. pp. 235-301.

Horowitz, A.J. 1985. A Primer on Trace Metal-Sediment Chemistry. U.S. Geological Survey Water Supply Paper 2277. U.S. Geological Survey, Alexandria, Virginia. 67 pp.

Houston, A.H. 1982. Thermal Effects Upon Fishes. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18566. 200 pp.

Hunn, J.B. and J.L. Allen. 1974. Movement of drugs across the gills of fishes. Annu. Rev. Pharmacol. 14: 47-55. (Cited in Zitko 1980.)

Hynes, H.B.N. 1970. The Ecology of Running Waters. University of Toronto Press, Toronto, Ontario. 555 pp.

IHP. 1982. Dispersion and Self-Purification of Pollutants in Surface Water Systems. A Contribution to the International Hydrological Program (IHP). P.G. Whitehead and T. Lack (eds.). IHP Working Group 6.1. United Nations Educational, Scientific and Cultural Organization, Paris, France. Tech. Pap. 23. 98 pp.

IJC. 1978. Annual Report to the International Joint Commission by the Great Lakes Research Advisory Board., Windsor, Ontario. 64 pp.

Jenne, E. 1976. Trace element sorption by sediments and soils – sites and processes. *In* Symposium on Molybdenum. Vol. 2. W. Chappell and K. Paterson (eds.). Marcel Dekker, New York. pp. 425-553. (Cited in Horowitz 1985.)

Jenne, E.A. and S.N. Luoma. 1977. Forms of trace elements in soils, sediments, and associated waters: an overview of their determination and biological activity. *In* Proc. Symp. on Biological Implications of Metals in the Environment, Energy Res. Dev. Admin. Symp. Ser. 42. pp. 110-143. (Cited in Demayo *et al*. 1978.)

Koch, R. 1984. Quantitative structure-activity relationships in ecotoxicology: possibilities and limits. *In* QSAR in Environmental Toxicology. K.L.E. Kaiser (ed.). Proc. Workshop on Quantitative Structure-Activity Relationships (QSAR) in Environmental Toxicology, McMaster University, Hamilton, Ontario, August 16-18, 1983. D. Reidel Publ. Co., Dordrecht, Holland. pp. 207-222.

Kramer, J.R. 1982. Alkalinity and acidity. *In* Water Analysis. Vol. I. Inorganic Species. Part I. R.A. Minear and L.H. Keith (eds.). Academic Press, Inc., New York. pp. 85-135.

Kranck, K. 1980. Sedimentation processes in the sea. *In* The Handbook of Environmental Chemistry. Vol. 2. Part A. Reactions and Processes. O. Hutzinger (ed.). Springer-Verlag, Berlin/Heidelberg, Germany. pp. 62-75.

Kwiatkowski, R.E. 1984. Lake Erie Review. *In* Statistical Assessment of the Great Lakes Surveillance Program, 1966-1981, Lake Erie. A.H. El-Shaarawi (ed.). National Water Research Institute. Inland Waters Directorate, Environment Canada, Burlington, Ontario. Scientific Series No. 136. pp. 3-26.

Lack, T.J. (ed.). 1984. Environmental Protection: Standards, Compliance and Costs. Ellis Horwood Ltd., West Sussex, England. 329 pp.

Laxen, D.P.H. 1983. The chemisiry of metal pollutants in water. *In* Pollution: Causes, Effects and Controls. 1983. R.M. Harrison (ed.). R. Soc. Chem., Burlington House, London. pp. 104-123.

Lech, J.J. and M.J. Vodicnik. 1985. Biotransformation. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill Publ. Book Co., New York. pp. 526-557.

Lee, G.F. and R.A. Jones. 1983. Translation of laboratory results to field conditions: the role of aquatic chemistry in assessing toxicity. *In* Aquatic Toxicology and Hazard Assessement. 6th Symp., ASTM Spec. Tech. Publ. 802. W.E. Bishop, R.D. Cardwell and B.B. Heidolph (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 328-349.

Leland, H.V. and J.S. Kuwabara. 1985. Trace metals. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 374-415.

Macan, T.T. 1974. Freshwater Ecology. Longman Group Ltd., London. 343 pp.

Mackay, D. 1980. Solubility, partition coefficients, volatility, and evaporation rates. *In* The Handbook of Environmental Chemistry. Vol. 2. Part A. Reactions and Processes. O. Hutzinger (ed.). Springer-Verlag, Berlin/Heidelberg, Germany. 307 pp.

Mackay, D. 1981. Environmental and laboratory rates of volatilization of toxic chemicals from water. *In* Hazard Assessment of Chemicals. Current Developments. Vol. 1. J. Saxena and F. Fisher (eds.). Academic Press, New York. pp. 303-322.

Mackay, D. 1982. Correlation of bioconcentration factors. Environ. Sci. Technol. 16: 274-278. (Cited in Connell and Miller 1984.)

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180. (Cited in Spencer and Farmer 1980.)

Mackay, D. and S. Paterson. 1982. Fugacity revisited. The fugacity approach to environmental transport. Environ. Sci. Technol. 16: 654A-660A.

Mackay, D. and S. Paterson. 1984. Spatial concentration distributions. Environ. Sci. Technol. 17: 207A-214A.

Mackay, D., W.Y. Shiu and R.J. Sutherland. 1980. Estimating volatilization and water column diffusion rates of hydrophobic contaminants. *In* Dynamics, Exposure and Hazard Assessment of

Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 127-142.

Matthess, G. 1985. Geochemical conditions in the ground water environment. *In* Planetary Geology. D.E. Caldwell, J.A. Brierley and C.L. Brierley (eds.). Van Nostrand Reinhold Co. Inc., New York. pp. 347-355.

Matthess, G. and J.C. Harvey. 1982. The Properties of Groundwater. John Wiley & Sons, Inc., New York. 406 pp.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.

Meyers, T.R. and J.D. Hendricks. 1985. Histopathology. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 283-331.

Mill, T. 1980. Data needed to predict the environmental fate of organic chemicals. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 297-322.

Moore, J.W. and S. Ramamoorthy. 1984. Organic Chemicals in Natural Waters. Applied Monitoring and Impact Assessment. Springer-Verlag, New York Inc., New York. p. 11.

Mullins, T. 1977. The chemistry of water pollution. *In* Environmental Chemistry. J.O. Bockris (ed.). Plenum Press, New York. pp. 331-400.

Neely, W.B. and G.E. Blau. 1985a. Environmental Exposure from Chemicals. Vol. I. Chemical Rubber Co. Press. Boca Raton, Florida.

Neely, W.B. and G.E. Blau. 1985b. Environmental Exposure from Chemicals. Vol. II. Chemical Rubber Co. Press. Boca Raton, Florida.

Neely, W.B., D.R. Branson and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113-1115. (Cited in Chiou 1982.)

Nicholson, B.C. 1984. Australian Water Quality Criteria for Organic Compounds. Australian Water Resources Council, Department of Resources and Energy. Australian Government Publ. Serv., Canberra, Australia. Tech. Pap. No. 82. 224 pp.

NRCC. 1981. A Screen for the Relative Persistence of Lipophilic Organic Chemicals in Aquatic Ecosystems – An Analysis of the Role of a Simple Computer Model in Screening. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC No. 18570. 304 pp.

O'Donnel, J.R., B.M. Kaplan and H.E. Allen. 1985. Bioavailability of trace metals in natural waters. *In* Aquatic Toxicology and Hazard Assessment. 7th Symp. ASTM Spec. Tech. Publ. 854. R.D. Cardwell, R. Purdy and R.C. Bahner (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 485-500.

Pagenkopf, G.K. 1978. Introduction to Natural Water Chemistry. Marcel Dekker, Inc., New York. 272 pp.

Rand, G.M. and S.R. Petrocelli. 1985. Introduction. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 1-28.

Ray, S.M. and N.M. Trieff. 1980. Bioaccumulation of anthropogenic toxins in the ecosystem. *In* Environment and Health. N.M. Trieff (ed.). Ann Arbor Science, Ann Arbor, Michigan. p. 93. (Cited in Connell and Miller 1984.)

Redfield, A.C., B.J. Ketchum and F.A. Richards. 1963. The influence of organisms on the composition of sea water. Vol. 2. *In* The Sea. M.N. Hill (ed.). Wiley-Interscience, New York. pp. 26-77. (Cited in Drever 1982.)

Reid, G.K. and R.D. Wood. 1976. Ecology of Inland Waters and Estuaries. D. Van Nostrand Co., New York. 485 pp.

Robertson, A. 1985. Development of ecosystem objectives for the Great Lakes. *In* Proc. Workshop on Limnology and Oceanography. International Joint Commission, June 1985, Minneapolis, Minnesota.

Russo, R.C. 1985. Ammonia, nitrite, and nitrate. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 455-471.

Ruttner, T. 1953. Fundamentals of Limnology. University of Toronto Press, Toronto, Ontario. 295 pp.

Schwartz, F.W. and P.A. Domenico. 1983. Simulation of hydrochemical patterns in regional groundwater flow. *In* Chemical Hydrogeology. W. Back and R.A. Freeze (eds.). Hutchinson Ross Publishing Co., Stroudsburg, Pennsylvania. pp. 370-383.

Spacie, A. and J.L. Hamelink. 1985. Bioaccumulation. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 495-525.

Spencer, W.F. and W.J. Farmer. 1980. Assessment of the vapor behavior of toxic organic chemicals. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 143-161.

Sprague, J.B. 1985. Factors that modify toxicity. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 124-163.

Stumm, W. and J.J. Morgan. 1970. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, Inc., New York. 583 pp.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2nd edition. John Wiley & Sons, Inc., New York. 780 pp.

Thurston, R.V., R.C. Russo and K. Emerson. 1979. Aqueous Ammonia Equilibrium – Tabulation of Percent Un-Ionized Ammonia. EPA Ecol. Res. Ser. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-79-091. p. iii. (Cited in Russo 1985.)

Todd, D.K. 1980. Groundwater Hydrology. 2nd edition. John Wiley & Sons, Inc. New York. 535 pp.

UNEP. 1985. Protection of the Marine Environment Against Pollution from Land-based Sources. Montreal Guidelines. United Nations Environment Programme (UNEP) Working Group of Experts on the Protection of the Marine Environment Against Pollution from Land-based Sources. Environ. Policy Law 14 (2/3): 77-83.

U.S. Department of the Interior. 1981. Ground-Water Manual. A Water Resources Technical Publication. A Guide for the Investigation, Development, and Management of Ground-Water Resources. John Wiley & Sons, Inc. New York. p. 4.

U.S. EPA. 1973. Water Quality Criteria 1972. Committee on Water Quality Criteria, U.S. Environmental Protection Agency, Washington, D.C. EPA-R3-73-033. 594 pp.

U.S. EPA. 1979. Water-related Environmental Fate of 129 Priority Pollutants. Vol. I. Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 2-1 – 2-16.

U.S. General Accounting Office. 1981. Better Monitoring Techniques Are Needed to Assess the Quality of Rivers and Streams. The Comptroller General Report to the Congress of the United States. Vol. II. CED.81.30. 121 pp.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York. pp. 1-135.

Waite, T.D. 1984. Principles of Water Quality. Academic Press, Inc. Orlando, Florida. 101 pp.

Warren, C.E. 1971. Biology and Water Pollution Control. W.B. Saunders Co., Philadelphia, Pennsylvania. 434 pp.

Westall, J. and W. Stumm. 1980. The hydrosphere. *In* The Handbook of Environmental Chemistry. Vol. I. Part A. The Natural Environment and Biochemical Cycles. O. Hutzinger (ed.). Springer-Verlag, New York. pp. 17-49.

Westman, W.E. 1985. Ecology, Impact Assessment, and Environmental Planning. John Wiley & Sons, New York. 532 pp.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.

Zepp, R.G. 1980. Assessing the photochemistry of organic pollutants in aquatic environment. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 69-110.

Zepp, R.G. and G.L. Baughman. 1978. Prediction of photochemical transformation of pollutants in the aquatic environment. *In* Aquatic Pollutants: Transformation and Biological Effects. O. Hutzinger, I.H. Van Lelyveld and B.C.J. Zoeteman (eds.). Proc. of the 2nd Int. Symp. on Aquatic Pollutants, Noordwijkerhout, Amsterdam, September 26-28, 1977. Pergamon of Canada Ltd., Toronto, Ontario. pp. 237-274.

Zitko, V. 1980. Metabolism and distribution by aquatic animals. *In* The Handbook of Environmental Chemistry. Vol. 2. Part A. Reactions and Processes. O. Hutzinger (ed.). Springer-Verlag, Berlin/Heidelberg, Germany. pp. 221-228.